

TABLE 4-3. STREAM DESIGNATIONS FOR FIGURE 4-5, PRODUCTION OF ETHYLENE FROM NAPHTHA AND/OR GAS-OIL FEEDS

| Stream Number | Stream Description |
|---------------|---|
| 1 | Naphtha or gas oil feed |
| 2 | Fuel gas and oil |
| 3 | Ethane/propane recycle stream |
| 4 | Cracked gas |
| 5 | Cracked gas |
| 6 | Recycled pyrolysis fuel oil from gasoline fractionator |
| 7 | Furnace exhaust |
| 8 | Slurry of collected furnace decoking particles |
| 9 | Quenched cracked gas |
| 10 | Surplus fuel oil |
| 11 | Light fractions |
| 12 | Overheads from gasoline fractionator |
| 13 | Condensed organic phase |
| 14 | Raw pyrolysis gasoline to intermediate storage |
| 15 | Water phase (saturated with organics) from quench tower |
| 16 | Recycled water phase from heat exchangers |
| 17 | Surplus water from quench tower |
| 18 | Wastewater blowdown from recycle steam generator |
| 19 | Overheads from quench tower |
| 20 | Water condensed during compression |
| 21 | Organic fractions condensed during compression |
| 22 | Acid gas stripped in amine stripper |
| 23 | Diethanolamine (DEA) |
| 24 | Liquid waste stream from caustic wash tower |
| 25 | Liquid waste stream from caustic wash tower |
| 26 | Process gas stream from caustic wash tower |
| 27 | Solid waste stream from drying traps |

TABLE 4-3. CONTINUED

| Stream Number | Stream Description |
|---------------|--|
| 28 | Process gas |
| 29 | Hydrogen rich stream from demethanizer |
| 30 | Methane rich stream from demethanizer |
| 31 | C ₂ components from de-ethanizer |
| 32 | C ₃ and heavier components from de-ethanizer |
| 33 | Hydrogenated acetylene from acetylene convertor |
| 34 | Overheads from ethylene fractionator |
| 35 | Ethane to recycle pyrolysis furnace |
| 36 | Overheads from depropanizer |
| 37 | Propylene (purified) |
| 38 | Propane to ethane/propane pyrolysis furnace |
| 39 | C ₄ and heavier components to debutanizer |
| 40 | Overheads from debutanizer |
| 41 | C ₅ and heavier components from debutanizer |
| 42 | Combined C ₅ components and gasoline stripper bottoms fractions |
| 43 | Light ends to cracked gas compressor |
| 44 | C ₅ and heavier components |
| 45 | Superheated stream |
| 46 | Stream and hydrocarbons |
| 47 | Organic vapor from separator pot |
| 48 | Organic vapor from separator pot |
| 49 | Organic vapor from separator pot |

which end pyrolysis and simultaneously generate steam. The streams from the transfer-line exchangers (Stream 5) are combined and further quenched by the injection of recycled pyrolysis fuel oil from the gasoline fractionator (Stream 6).

The remaining operations shown in Figure 4-5 are required for separation of the various product fractions formed in the cracking of gas oil and/or naphtha; for removal of acid gases (primarily hydrogen sulfide [H₂S]) and carbon dioxide (CO₂) and water; and for hydrogenation of acetylene compounds to olefins or paraffins.

The quenched cracked gas (Stream 9) passes to the gasoline fractionator, where pyrolysis fuel oil is separated. Most of the fuel oil passes through water-cooled heat exchangers and is recycled (Stream 6) to the preceding oil-quenching operation. The surplus fuel oil (Stream 10), equivalent to the quantity initially present in the cracked gas, passes first to the fuel oil stripper, where light fractions are removed, and then to fuel oil storage. The light fractions (Stream 11) removed in the fuel oil stripper are recycled to the gasoline fractionator. The gasoline fractionator temperatures are well above the vaporization temperature of water, and the contained water remains as superheated steam, with the overhead stream containing the lighter cracked-gas components.

The overhead stream from the gasoline fractionator (Stream 12) passes to the quench tower, where the temperature is further reduced, condensing most of the water and part of the C₅ and heavier compounds. The condensed organic phase (Stream 13) is stripped of the lighter components in the gasoline stripper and is passed to raw pyrolysis gasoline intermediate storage (Stream 14). Most of the water phase, which is saturated with organics, is separated in the quench tower (Stream 15), passed through water-cooled heat exchangers (Stream 16), and then recycled to the quench tower to provide the necessary cooling. The surplus water (Stream 17), approximately equivalent to the quantity of steam injected with the pyrolysis furnace feed, passes to the dilution steam generator, where it is vaporized and recycled as steam to the pyrolysis furnaces. Blowdown from the recycle steam generator is removed as a wastewater stream (Stream 18).

On leaving the quench tower, the pyrolysis gas is compressed to about 3.5 mPa in five stages.²⁹ The overhead stream from the quench tower (Stream 19) passes to a centrifugal charge-gas compressor (first three stages), where it is compressed. Water (Stream 20) and organic fractions (Stream 21) condensed during compression and cooling are recycled to the quench tower and gasoline stripper.

Lubricating oil (seal oil) discharged from the charge-gas compressor is stripped of volatile organics in a separator pot before the oil is recirculated. The organic vapor is vented to the atmosphere (Vent G). Similar separator pots separate volatile organics from lubricating oil from both the ethylene and propylene refrigeration compressors (Streams 48 and 49).

Following compression, acid gas (H_2S and CO_2) is removed by absorption in diethanolamine (DEA) or other similar solvents in the amine wash tower followed by a caustic wash step. The amine stripper strips the acid gas (Stream 22) from the saturated DEA and the DEA (Stream 23) is recycled to the amine wash tower. Very little blowdown from the DEA cycle is required.

The waste caustic solution, blowdown from the DEA cycle, and wastewater from the caustic wash tower are neutralized, stripped of acid gas, and removed as liquid waste streams (Streams 24 and 25). The acid gas stripped from the DEA and caustic waste (Stream 22) passes to an emission control device (Vent D), primarily to control H_2S emissions.

Following acid gas removal, the remaining process gas stream (Stream 26) is further compressed and passed through drying traps containing a desiccant, where the water content is reduced to the low level necessary to prevent ice or hydrate formation in the low-temperature distillation operations. The drying traps are operated on a cyclic basis, with periodic regeneration necessary to remove accumulated water from the desiccant. The desiccant is regenerated with heated fuel gas and the effluent gas is routed to the fuel system. Fouling of the desiccant by polymer formation necessitates periodic desiccant replacement,

which results in the generation of a solid waste (Stream 27). However, with a normal desiccant service life of possibly several years, this waste source is relatively minor.

With the exception of three catalytic hydrogenation operations, the remaining process steps involve a series of fractionations in which the various product fractions are successively separated.

The demethanizer separates a mixture of hydrogen and methane from the C_2 and heavier components of the process gas (Stream 28). The demethanizer overhead stream (hydrogen and methane) is further separated into hydrogen-rich and methane-rich streams (Streams 29 and 30) in the low-temperature chilling section. The methane-rich stream is used primarily for furnace fuel. Hydrogen is required in the catalytic hydrogenation operations.

The de-ethanizer separates the C_2 components (ethylene, ethane, and acetylene) (Stream 31) from the C_3 and heavier components (Stream 32). Following catalytic hydrogenation of acetylene to ethylene by the acetylene converter (Stream 33), the ethylene-ethane split is made by the ethylene fractionator. The overhead from the ethylene fractionator (Stream 34) is removed as the purified ethylene product, and the ethane fraction (Stream 35) is recycled to the ethane/propane cracking furnace. For the separation of binary mixtures with close boiling points, such as in the ethylene-ethane fractions, open heat pumps are thermodynamically the most attractive. Both heating and cooling duties have to be incorporated into the cascade refrigeration system for optimum energy utilization.²⁹

The de-ethanizer bottoms (C_3 and heavier compounds) (Stream 32) pass to the depropanizer, where a C_3 - C_4 split is made. The depropanizer overhead stream (primarily propylene and propane) (Stream 36) passes to a catalytic hydrogenation reactor (C_3 converter), where traces of propadiene and methyl acetylene are hydrogenated. Following hydrogenation, the C_3 fraction passes to the propylene fractionator, where propylene is removed overhead as a purified product (Stream 37). The propane (Stream 38) is recycled to the ethane/propane pyrolysis furnace.

The C₄ and heavier components (Stream 39) from the depropanizer pass to the debutanizer, where a C₄-C₅ split is made. The overhead C₄ stream (Stream 40) is removed as feed to a separate butadiene process.

The stream containing C₅ and heavier compounds from the debutanizer (Stream 41) is combined with the bottoms fraction from the gasoline stripper as raw pyrolysis gasoline. The combined stream (Stream 42) is hydrogenated in the gasoline treatment section. Following the stripping of lights (Stream 43), which are recycled to the cracked-gas compressor, the C₅ and heavier compounds (Stream 44) are transferred to storage as treated pyrolysis gasoline. This stream contains benzene and other aromatics formed by pyrolysis.

The three catalytic hydrogenation reactors for acetylene, C₃ compounds, and pyrolysis gasoline all require periodic regeneration of the catalyst to remove contaminants. The catalyst is generally regenerated every four to six months. At the start of regeneration, as superheated steam (Stream 45) is passed through a reactor, a mixture of steam and hydrocarbons leaving the reactor (Stream 46) is passed to the quench tower. After sufficient time has elapsed for stripping of organics (approximately 48 hours), the exhaust is directed to an atmospheric vent (Vent F) and a steam-air mixture is passed through the catalyst to remove residual carbon. This operation continues for an additional 24 to 48 hours. The presence of air during this phase of the regeneration prevents the vented vapor from being returned to the process.

Because the olefins and di-olefins present in pyrolysis gasoline are unstable in motor gasoline and interfere with extraction of aromatics, they are hydrogenated prior to extraction of aromatics.¹⁰ Also, as mentioned before, because the benzene content of pyrolysis gasoline can be high, some plants recover motor gasoline, aromatics (BTX), or benzene from the pyrolysis gasoline.

Recovery of Benzene from Pyrolysis Gasoline

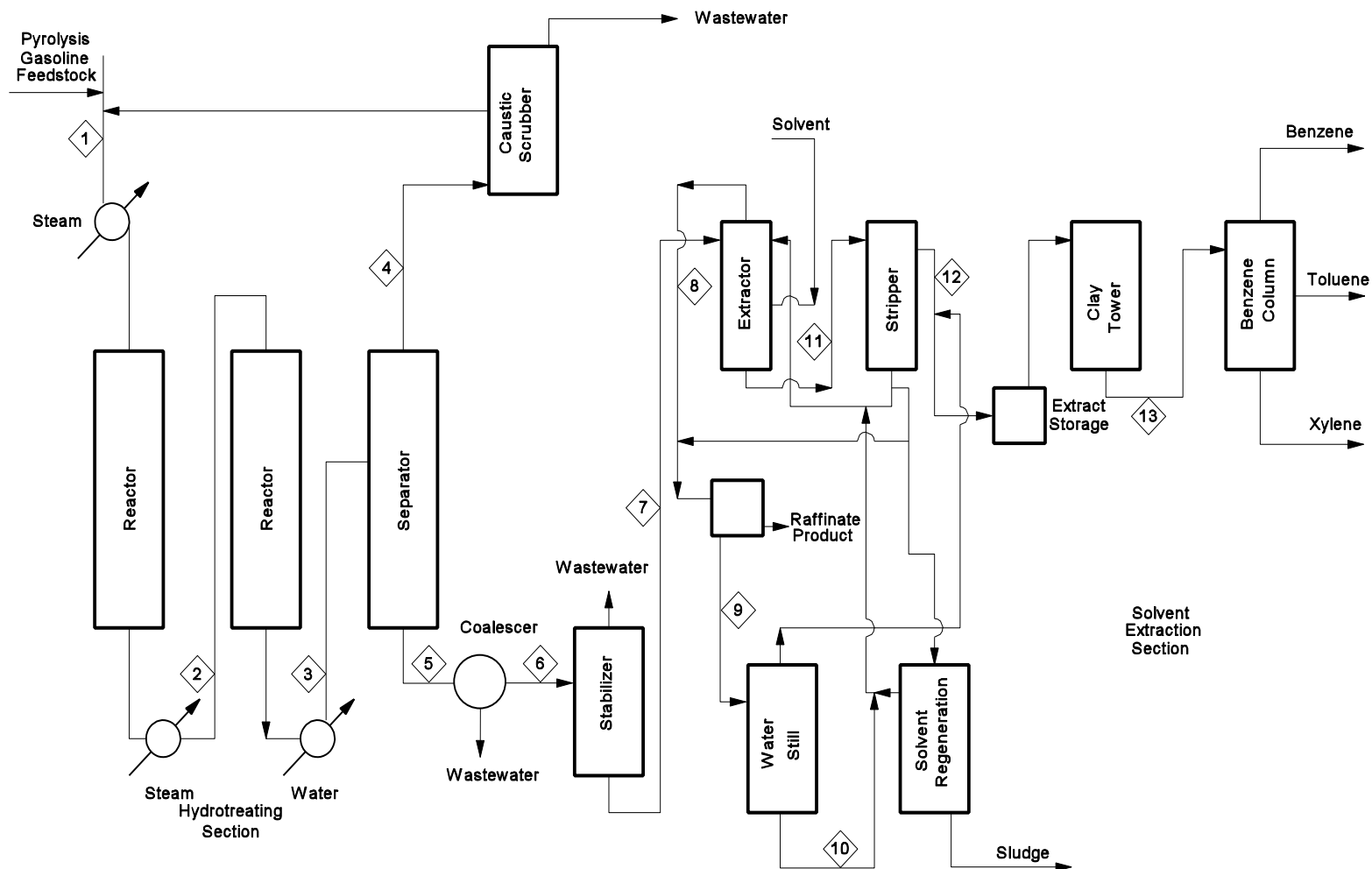
A process flow diagram for a plant producing benzene, toluene, and xylenes by hydrogenation of pyrolysis gasoline is presented in Figure 4-6. Pyrolysis gasoline is fed with make-up hydrogen into the first stage hydrogenation reactor (Stream 1), where olefins are hydrogenated. The reaction conditions are mild (104 to 203 °F [40 to 95 °C] and 147 to 588 lb/in² [10 to 40 atmospheres pressure]).¹⁰

The catalyst in the first stage reactor (nickel or palladium) requires more frequent regeneration than most refinery catalysts because of the formation of gums. Catalyst may be regenerated about every 4 months and coke is burned off every 9 to 12 months.^{10,30}

From the first reactor, the hydrogenated di-olefins and olefins are sent to a second reactor (Stream 2). Reactor effluent is then cooled and discharged into a separator (Stream 3). Part of the gas stream from the separator is recycled back to the reactor (Stream 4) after being scrubbed with caustic solution. The liquid phase from the separator is sent to a coalescer (Stream 5), where water is used to trap particles of coke formed in the reactor.³⁰ Next, the light hydrocarbons are removed from the liquid in the stabilizer (Stream 6). At this point, the process becomes similar to the solvent extraction of reformat in the catalytic reforming of naphtha. The stabilized liquid is extracted with a solvent, usually Sulfolane or tetraethylene glycol (Stream 7).

The raffinate (Stream 8) contains paraffins and may be sent to a cracking furnace to produce olefins.³⁰ The solvent may be regenerated (Streams 9 and 10). Dissolved aromatics (benzene, toluene, and xylene) are separated from the solvent by distillation (Stream 11) and sent through clay towers (Stream 12). Individual components (benzene, toluene, and xylene) are finally separated (Stream 13) and sent to storage.

The above process may vary among facilities. For example, Stream 1 may be passed over additional catalyst, such as cobalt molybdenum, after being passed over a nickel or



Note: No data were available concerning benzene emission points. Likely emission points include reactor vents, compressors, and any vents on the benzene column.

Figure 4-6. Production of BTX by Hydrogenation of Pyrolysis Gasoline

Source: Reference 30.

palladium catalyst. Also, the olefins produced from the raffinate stream (Stream 8) may be added to a gasoline process or sold as a reformer stock.³¹

4.3.2 Benzene Emissions from Ethylene Plants and Benzene Recovery from Pyrolysis Gasoline

Production of ethylene from naphtha/gas oil does not produce large quantities of volatile organic compounds (VOC) or benzene emissions from process vents during normal operations.²⁸ Emission factors for benzene from sources at ethylene plants are shown in Table 4-4. The chief source of benzene emissions during normal operations is the charge gas compressor lubricating oil vent (Stream 47, Vent G in Figure 4-5). The emission factors in Table 4-4 were developed from data supplied by ethylene manufacturers.

Most benzene emissions from ethylene plants are intermittent and occur during plant startup and shutdown, process upsets, and emergencies (Vent E). For example, benzene may be emitted from pressure relief devices, during intentional venting of off-specification materials, or during depressurizing and purging of equipment for maintenance.²⁸ Charge gas compressor and refrigeration compressor outages are also potential sources. Emissions from these compressors are generally short term in duration, but pollutants may be emitted at a high rate.

In general, intermittent emissions and emissions from all pressure relief devices and emergency vents are routed through the main process vent (Vent E in Figure 4-5). The vent usually is controlled. The relief valve from the demethanizer is usually not routed to the main vent, but the valve is operated infrequently and emits mainly hydrogen and methane.²⁸

Potential sources of benzene such as flue gas from the cracking furnace (Vent A), pyrolysis furnace decoking (Vent B), acid gas removal (Vent D), and hydrogenation catalyst regeneration (Vent F) generally are not significant sources.²⁸ Flue gas normally contains products of hydrogen and methane combustion. Emissions from pyrolysis furnace decoking consist of air, steam, CO₂, CO, and particles of unburned carbon.²⁸ Emissions from

TABLE 4-4. BENZENE EMISSION FACTORS FOR A HYPOTHETICAL ETHYLENE PLANT^a

| SCC and Description | Emission Source | Control Device | Emission Factor in lb/ton (kg/Mg) | Factor Rating |
|---|--------------------------------|-----------------------------------|-----------------------------------|---------------|
| 3-01-197-45 Ethylene Manufacturing-Compressor Lube Oil Vent | Compressor Lube Oil Vents | Uncontrolled | 0.0006 (0.0003) | U |
| | Single Compressor Train | Uncontrolled | 0.0004 (0.0002) | U |
| | Dual Compressor Train | Uncontrolled | 0.0008 (0.0004) | U |
| 3-01-197-42 Ethylene Manufacturing - Pyrolysis Furnace Decoking | Pyrolysis Furnace Decoking | | No benzene emissions | |
| 3-01-197-43 Ethylene Manufacturing-Acid Gas Removal | Acid Gas Removal | | No benzene emissions | |
| 3-01-197-44 Ethylene Manufacturing - Catalyst Regeneration | Catalyst Regeneration | | No benzene emissions | |
| 3-01-197-XX Ethylene Manufacturing - Secondary Sources | Secondary Wastewater Treatment | Uncontrolled | 0.0434 (0.0217) | U |
| 3-01-197-49 Ethylene Manufacturing - Equipment Leak Emissions | Equipment Leak Emissions | Detection/ Correction of leaks | See Section 4.5.2 | |
| | | Uncontrolled | See Section 4.5.2 | |

TABLE 4-4. BENZENE EMISSION FACTORS FOR A HYPOTHETICAL ETHYLENE PLANT^a

| SCC and Description | Emission Source | Control Device | Emission Factor in lb/ton (kg/Mg) | Factor Rating |
|--|-------------------------------------|----------------|-----------------------------------|---------------|
| 3-01-197-XX Ethylene Manufacturing- Intermittent Emissions | Intermittent Emissions ^c | | | |
| | Single Compressor Train | Flare | 0.1584-0.0316 (0.0792-0.0158) | U |
| | | Uncontrolled | 1.584 (0.7919) | U |
| | Dual Compressor Train | Flare | 0.0202-0.004 (0.0101-0.002) | U |
| | | Uncontrolled | 0.2022 (0.1011) | U |

^a Data are for a hypothetical plant using 50 percent naphtha/50 percent gas oil as feed and having an ethylene capacity of 1,199,743 lb/yr (544.2 Gg/yr).

^b Factors are expressed as lb (kg) benzene emitted per ton (Mg) ethylene produced.

^c Intermittent emissions have been reported from the activation of pressure relief devices and the depressurization and purging of equipment for maintenance purposes.

acid gas removal are H_2S , SO_2 , and CO_2 ; these emissions are generally controlled to recover H_2S as sulfur or convert H_2S to SO_2 . As discussed earlier, catalyst regeneration is infrequent and no significant concentrations of benzene have been reported as present in the emissions.²⁸

Equipment leak benzene emissions at ethylene plants may originate from pumps, valves, process sampling, and continuous process analysis. Refer to Section 4.5.2 of this document, for information on emission estimates procedures, and available emission factors. Regarding equipment leak component counts, totals of 377 and 719 valves for benzene vapor and benzene liquid service respectively had been reported for ethylene plants.³² Storage of ethylene in salt domes is not a potential source of benzene emissions because the ethylene generally does not contain benzene.

The emission factor for benzene from storage vessels shown in Table 4-4 was derived from AP-42 equations.³³ No supporting data showing how the equations were applied were provided by the emission factor reference.

Secondary emissions include those associated with handling and disposal of process wastewater. The emission factor in Table 4-4 was derived from estimates of wastewater produced and the estimated percent of the volatile organic compounds (VOC) emitted from the wastewater that is benzene.

No data were available concerning benzene emissions from recovering benzene from pyrolysis gasoline. Likely sources include reactor vents, compressors, and any vents on the benzene column (Figure 4-6).

The primary control techniques available for intermittent emissions of benzene (pressure relief valves, emergency vents) are flaring and combustion within industrial waste boilers. Other control methods are not as attractive because the emissions are infrequent and of short duration. The estimated control efficiency of flares is 98 percent or greater³⁴ while control efficiencies for industrial waste boilers vary depending upon design and operation.²⁸

For additional discussion on flares and industrial waste boilers as control methods, see Section 4.5.1. One ethylene producer that provided a process description stated that all process vents are connected to flares. However, it was not possible to determine how prevalent such systems are for ethylene production.³⁵

Equipment leak emissions may be controlled by inspection/maintenance plans or use of equipment such as tandem seal pumps. For additional discussion on equipment leak emissions, see Section 4.5.2. Emissions from sampling lines can be controlled by piping sample line purge gas to the charge gas compressor or to a combustion chamber. Streams from process analyzers may be controlled in the same manner.²⁸

The primary means of controlling emissions from pyrolysis gasoline or naphtha feedstock storage is floating roof tanks. Emissions can be reduced by 85 percent when internal floating roof devices are used.²⁸ For additional discussion on storage tank emissions, see Section 4.5.3.

4.4 COKE OVEN AND COKE BY-PRODUCT RECOVERY PLANTS

Most coke is produced in the U.S. using the by-product recovery process. In 1994, there was one plant that used a “nonrecovery” process. This section will focus on the by-product recovery process because there are so few nonrecovery facilities in operation.²⁹⁶

4.4.1 Process Description

Although most benzene is obtained from petroleum, some is recovered through distillation of coke oven light oil at coke by-product recovery plants. Light oil is a clear yellow-brown oil that contains coke oven gas components with boiling points between 32 and 392°F (0 and 200°C).²⁶ Most by-product recovery plants recover light oil, but not all plants refine it. About 3.4 to 4.8 gal (13 to 18 liters [L]) of light oil can be recovered from the coke

oven gas evolved in coke ovens producing 0.91 ton (1 megagram [Mg]) of furnace coke (3 to 4 gal/ton [10.3 to 13.7 L/Mg]). Light oil itself is 60 to 85 percent benzene.³⁷

The coke by-product industry recovers various components of coke oven gas including:

- Coal tar, a feedstock for producing electrode binder pitch, roofing pitch, road tar, and numerous basic chemicals;
- Light oil, a source of benzene and other light aromatic chemicals;
- Ammonia or ammonium sulfate, for agriculture and as chemical feedstocks;
- Sulfur, a basic chemical commodity;
- Naphthalene, used primarily as an intermediate in the production of organic chemicals; and
- Coke oven gas, a high-quality fuel similar to natural gas.³⁸

Because it is contained in the coke oven gas, benzene may be emitted from processes at by-product recovery plants that do not specifically recover or refine benzene. Table 4-5 lists coke oven batteries with by-product recovery plants in the United States.³⁶ Figure 4-7 shows a process flow diagram for a representative coke by-product recovery plant.^{37,39} The figure does not necessarily reflect any given plant, nor does it include all possible operations that could be found at a given facility. The number of units and the types of processes used varies among specific plants. For example, naphthalene recovery is not practiced at all plants, and some plants do not separate benzene from the light oil. Therefore, it is advisable to contact a specific facility to determine which processes are used before estimating emissions based on data in this document.

Coal is converted to coke in coke ovens. About 99 percent of the U.S. production of coke uses the slot oven process, also referred to as the Kopper-Becker by-product coking process; the other 1 percent is produced in the original beehive ovens.

TABLE 4-5. COKE OVEN BATTERIES CURRENTLY OPERATING
IN THE UNITED STATES

| Plant (Location) | Battery Identification Number |
|------------------------------------|----------------------------------|
| ABC Coke (Tarrant, AL) | A 5 6 |
| Acme Steel (Chicago, IL) | 1 2 |
| Armco, Inc. (Middletown, OH) | 1 2 3 |
| Armco, Inc. (Ashland, KY) | 3 4 |
| Bethlehem Steel (Bethlehem, PA) | A 2 3 |
| Bethlehem Steel (Burns Harbor, IN) | 1 2 |
| Bethlehem Steel (Lackawanna, NY) | 7 8 |
| Citizens Gas (Indianapolis, IN) | E H 1 |
| Empire Coke (Holt, AL) | 1 2 |
| Erie Coke (Erie, PA) | A B |
| Geneva Steel (Provo, UT) | 1 2 3 4 |
| Gulf States Steel (Gadsden, AL) | 2 3 |

TABLE 4-5. CONTINUED

| Plant (Location) | Battery Identification Number |
|-----------------------------------|--------------------------------|
| Inland Steel (East Chicago, IN) | 6 7 9 10 11 |
| Koppers (Woodward, AL) | 1 2A 2B 4A 4B 5 |
| LTV Steel (Cleveland, OH) | 6 7 |
| LTV Steel (Pittsburgh, PA) | P1 P2 P3N P3S P4 |
| LTV Steel (Chicago, IL) | 2 |
| LTV Steel (Warren, OH) | 4 |
| National Steel (Ecorse, MI) | 5 |
| National Steel (Granite City, IL) | A B |
| New Boston Coke (Portsmouth, OH) | 1 |
| Sharon Steel (Monessen, PA) | 1B 2 |
| Shenango (Pittsburgh, PA) | 1 4 |
| Sloss Industries (Birmingham, AL) | 3 4 5 |
| Toledo Coke (Toledo, OH) | C |
| Tonawanda Coke (Buffalo, NY) | 1 |

TABLE 4-5. CONTINUED

| Plant (Location) | Battery Identification Number |
|---|-------------------------------|
| USX (Clairton, PA) | 1 |
| | 2 |
| | 3 |
| | 7 |
| | 8 |
| | 9 |
| | 13 |
| | 14 |
| | 15 |
| | 19 |
| | 20 |
| | B |
| | |
| USX (Gary, IN) | 23 |
| | 5 |
| | 7 |
| Wheeling-Pittsburgh (East Steubenville, WV) | 1 |
| | 2 |
| | 3 |
| | 8 |

Source: Reference 36.

NOTE: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current lists and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel. These operating plants and locations were current as of April 1, 1992.

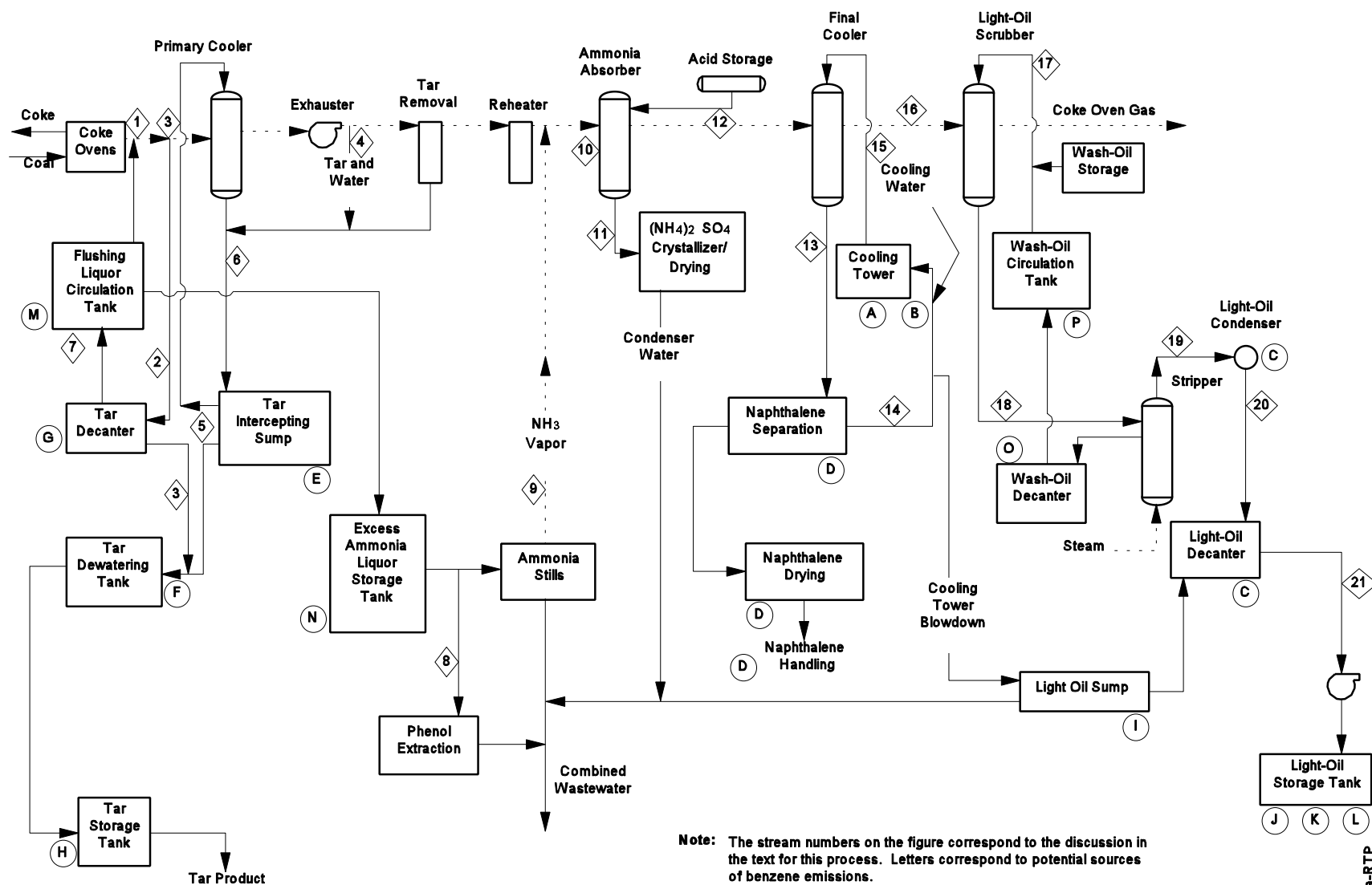


Figure 4-7. Coke Oven By-Product Recovery, Representative Plant

Source: Reference 37 and 39.

Each oven has 3 main parts: coking chambers, heating chambers, and regenerative chambers. All of the chambers are lined with refractory (silica) brick. The coking chamber has ports in the top for charging of the coal.²²

Each oven is typically capable of producing batches of 10 to 55 tons (9.1 to 49.9 Mg) of coke product. A coke oven battery is a series of 20 to 100 coke ovens operated together, with offtake flues on either end of the ovens to remove gases produced. The individual ovens are charged and discharged at approximately equal time intervals during the coke cycle. The resulting constant flow of evolved gas from all the ovens in a battery helps to maintain a balance of pressure in the flues, collecting main, and stack. Process heat comes from the combustion of gases between the coke chambers. Approximately 40 percent of cleaned oven gas (after the removal of its byproducts) is used to heat the coke ovens. The rest is either used in other production processes related to steel production or sold. Coke oven gas is the most common fuel for underfiring coke ovens.²² The coking time affects the type of coke produced. Furnace coke results when coal is coked for about 15 to 18 hours. Foundry coke, which is less common and is of higher quality (because it is harder and less readily ignited), results when coal is coked for about 25 to 30 hours.³⁷

The coking process is actually thermal distillation of coal to separate volatile and nonvolatile components. Pulverized coal is charged into the top of an empty, but hot, coke oven. Peaks of coal form under the charging ports and a leveling bar smoothes them out. After the leveling bar is withdrawn, the topside charging ports are closed and the coking process begins.

Heat for the coke ovens is supplied by a combustion system under the coke oven. The gases evolved during the thermal distillation are removed through the offtake main and sent to the by-product recovery plant for further processing.

After coking is completed (no volatiles remain), the coke in the chamber is ready to be removed. Doors on both sides of the chamber are opened and a ram is inserted into the chamber. The coke is pushed out of the oven in less than 1 minute, through the coke guide and into a quench car. After the coke is pushed from the oven, the doors are cleaned and repositioned. The oven is then ready to receive another charge of coal.

The quench car carrying the hot coke moves along the battery tracks to a quench tower where approximately 270 gallons of water per ton of coke (1,130 L of water per Mg) are sprayed onto the coke mass to cool it from about 2000 to 180 °F (1100 to 80 °C) and to prevent it from igniting. The quench car may rely on a movable hood to collect particulate emissions, or it may have a scrubber car attached. The car then discharges the coke onto a wharf to drain and continue cooling. Gates on the wharf are opened to allow the coke to fall onto a conveyor that carries it to the crushing and screening station. After sizing, coke is sent to the blast furnace or to storage.

As shown in Figure 4-7, coke oven gas leaves the oven at about 1292 °F (700 °C) and is immediately contacted with flushing liquor (Stream 1). The flushing liquor reduces the temperature of the gas and acts as a collecting medium for condensed tar. The gas then passes into the suction main. About 80 percent of the tar is separated from the gas in the mains as “heavy” tar and is flushed to the tar decanter (Stream 2).³⁷ Another 20 percent of the tar is “light” tar, which is cleaner and less viscous, and is condensed and collected in the primary cooler.³⁹ Smaller amounts of “tar fog” are removed from the gas by collectors (electrostatic precipitators or gas scrubbers) (Stream 4).³⁷ Light tar and tar fog is collected in the tar intercept sump (stream 6) and is routed to the tar decanter (Stream 5).

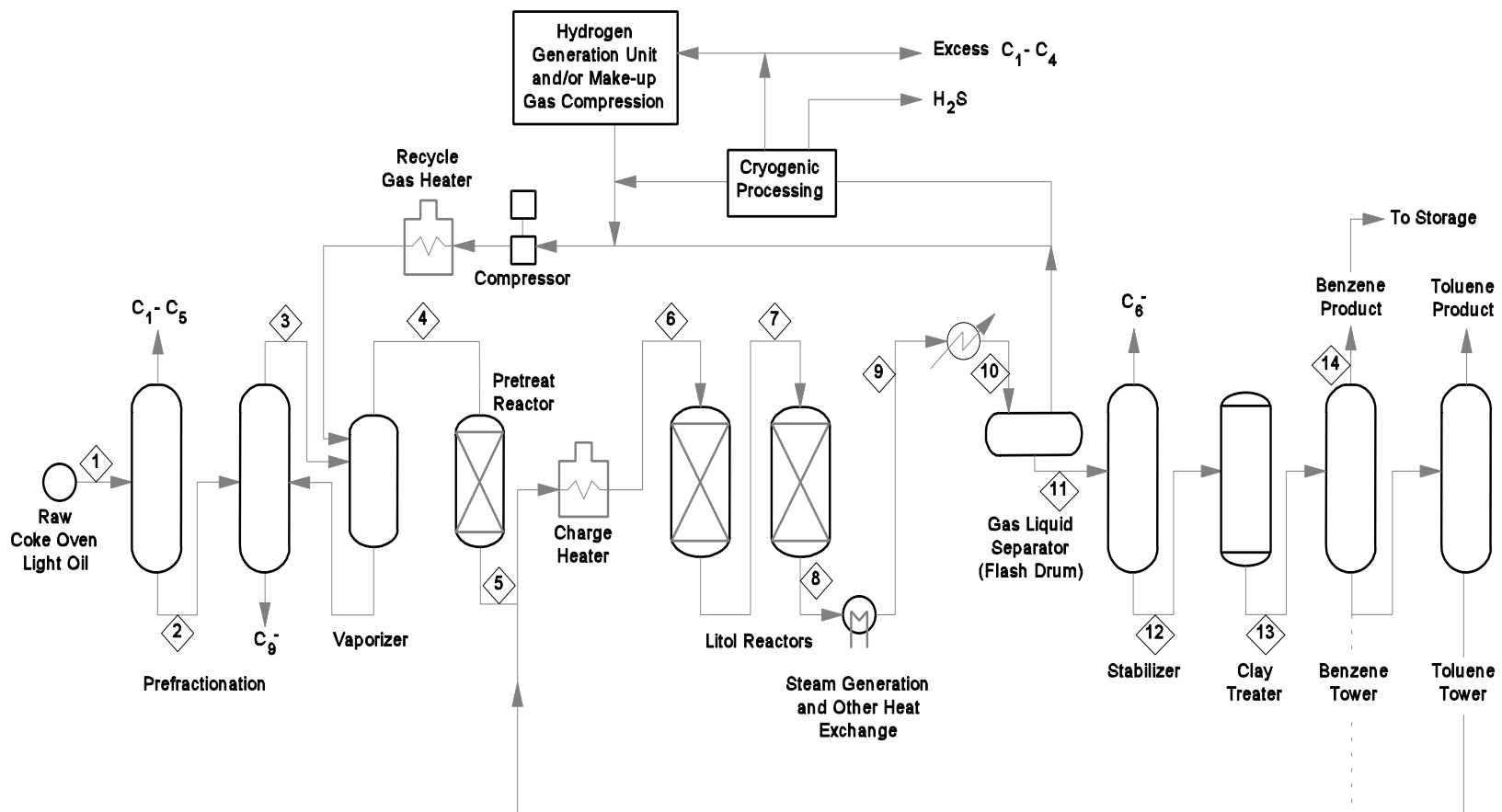
Depending on plant design, the heavy and light tar streams (Streams 2 and 5) may be merged or separated. The tar is separated from the flushing liquor by gravity in the tar decanter. Recovered flushing liquor is returned to the Flushing Liquor Circulation Tank (Stream 7) and re-used. Tar from the decanter is further refined in the tar dewater tank

(Stream 3). Tar may be sold to coal tar refiners or it may be refined further on site. Tar and tar products are stored on site in tanks.

Wastewater processing can recover phenol (Stream 8) and ammonia, with the ammonia routinely being reinjected into the gas stream (Stream 9). Ammonia salts or ammonia can be recovered by several processes. Traditionally, the ammonia-containing coke oven gas is contacted with sulfuric acid (Stream 10), and ammonium sulfate crystals are recovered (Stream 11). The coke oven gas from which tar and ammonia have been recovered is sent to the final cooler (Stream 12). The final cooler is generally a spray tower, with water serving as the cooling medium.³⁷

Three types of final coolers and naphthalene recovery technologies are currently used: (1) direct cooling with water and naphthalene recovery by physical separation, (2) direct cooling with water and naphthalene recovery in the tar bottom of the final cooler, and (3) direct cooling with wash oil and naphthalene recovery in the wash oil.³⁷ Most plants use direct water final coolers and recover naphthalene by physical separation.³⁷ In this method, naphthalene in the coke oven gas is condensed in the cooling medium and separated by gravity (Stream 13). After the naphthalene is separated, the water is sent to a cooling tower (Stream 14) and recirculated to the final cooler (Stream 15). The coke oven gas that leaves the final cooler is sent to the light oil processing segment of the plant (Stream 16).

As shown in Figure 4-7, light oil is primarily recovered from coke oven gas by continuous countercurrent absorption in a high-boiling liquid from which it is stripped by steam distillation.¹⁰ Coke oven gas is introduced into a light oil scrubber (Stream 16). Packed or tray towers have been used in this phase of the process, but spray towers are now commonly used.¹⁰ Wash oil is introduced into the top of the tower (Stream 17) and is circulated through the contacting stages of the tower at around 0.11 to .019 gal/ft³ (1.5 to 2.5 liters per cubic meter [L/m³]) of coke oven gas.³⁹ At a temperature of about 86 °F (30 °C), a light oil scrubber will remove 95 percent of the light oil from coke oven gas. The



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 4-8. Litol Process Flow Diagram

Source: References 40 and 41.

benzene-containing wash oil is steam-stripped (Stream 18) to recover the light oil.³⁹ Steam and stripped vapors are condensed and separated (Streams 19 and 20). The light oil is sent to storage (Stream 21).^{37,39}

To recover the benzene present in the light oil, processes such as Litol (licensed by Houdry) or Hydeal (licensed by UOP) are used. Figure 4-8 shows a process diagram of the Litol process. The following discussion of the Litol process is drawn from two published descriptions of the process.^{40,41}

The light oil is prefractionated (Stream 1) to remove the C₅ and lighter fractions, and the C₉ and heavier fractions (Stream 2). The remaining “heart cut” is sent to a vaporizer, where it contacts gas with a high hydrogen content (Stream 3). The light oil and hydrogen then flow to a pretreat reactor (Stream 4), where styrene, di-olefins, and some sulfur compounds are hydrogenated (at about 572°F [300°C]). The partially hydrogenated stream is heated by the charge heater to the temperature required for the main reactor (Stream 5).

The stream is then sent through a set of fixed-bed (Litol) reactors (Streams 6 and 7), where all remaining sulfur compounds are converted to H₂S and organics are dehydrogenated or dealkylated. The reactor effluent is cooled by post-reactor exchangers (Streams 8 and 9). At the flash drum, aromatics are condensed and separated from the gas stream (Stream 10). At the stabilizer, additional gas is removed, resulting in a hot liquid fuel for clay treatment (Stream 11). The clay treater removes the last trace of unsaturates from the aromatics (Stream 12). Conventional distillation yields pure benzene followed by pure toluene (Stream 13). Benzene product may then be sent to storage (Stream 14).^{40,41}

4.4.2 Benzene Emissions

Benzene may be emitted from many points in a coke and coke by-product plant; emissions are not limited to the benzene recovery section of the process. The coke

ovens themselves are potential sources of benzene emissions from the charging operation, leaking coke oven doors, topside port lids and offtake systems on the topside of the battery, collecting mains, and bypass/bleeder stacks.³⁶

During charging, moist coal contacts the hot oven floor and walls and, as a result, the release of volatile components begins immediately. Control of charging emissions is more dependent on operating procedures than on equipment. Control options include staged charging, sequential charging, and use of wet scrubbers on larry cars (the mobile hoppers that discharge the coal).

Staged charging involves pouring coal into the coke ovens so that an exit space for the generated gases is constantly maintained.⁴² The hoppers delivering the coal are discharged such that emissions are contained in the ovens and collecting mains by steam aspiration. Generally, a maximum of two hoppers are discharging at the same time.

In sequential charging, the first hoppers are still discharging when subsequent hoppers begin discharging coal. As with staged charging, the coke ovens are under aspiration in sequential charging. The sequential charging procedure is designed to shorten the charging time.

In the use of wet scrubbers on larry cars, the scrubber emissions are contained by hoods or shrouds that are lowered over the charging ports.

Another potential source of benzene emissions at coke ovens is leaking doors. The doors are sealed before the coking process begins. Some doors have a flexible metal band or rigid knife edge as a seal. The seal is formed by condensation of escaping tars on the door's metal edge. Other doors are sealed by hand by troweling a mixture into the opening between the coke oven door and door frame. After the coking process is complete, the doors are opened to push the coked coal out into special railroad cars called quench cars for transport to the quench tower. Quenched coke is then discharged onto a "coke wharf" to

allow quench water to drain and to let the coke cool. Control techniques for leaking doors include oven door seal technology, pressure differential devices, hoods/shrouds over the doors, and the use of more efficient operating/maintenance procedures.⁴²

Oven door seal technology relies on the principle of producing a resistance to the flow of gases out of the coke oven. This resistance may be produced by a metal-to-metal seal, a resilient soft seal, or a luted seal (applying a slurry mixture of clay, coal, and other materials). Small cracks and defects in the seal allow pollutants to escape from the coke oven early in the cycle. The magnitude of the leak is determined by the size of the opening, the pressure drop between the oven and the atmosphere, and the composition of the emissions.

The effectiveness of a pressure differential control device depends on the ability of the device to reduce or reverse the pressure differential across any defects in the door seal. These systems either provide a channel to permit gases that evolve at the bottom of the oven to escape to the collecting main, or the systems provide external pressure on the seal through the use of steam or inert gases.

Oven door emissions also can be reduced by collecting the leaking gases and particulates and subsequently removing these pollutants from the air stream. A suction hood above each door with a wet electrostatic precipitator for fume removal is an example of this type of system.

Other control techniques rely on operating and maintenance procedures rather than only hardware. Operating procedures for emission reduction could include changes in the oven cycle times and temperatures, the amount and placement of each charge, and any adjustments of the end-door while the oven is on line. Maintenance procedures include routine inspection, replacement, and repair of control devices and doors.

Topside leaks are those occurring from rims of charging ports and standpipe leaks on the top of the coke oven. These leaks are primarily controlled by proper maintenance and operating procedures that include:⁴²

- Replacement of warped lids;
- Cleaning carbon deposits or other obstructions from the mating surfaces of lids or their seats;
- Patching or replacing cracked standpipes;
- Sealing lids after a charge or whenever necessary with lute; and
- Sealing cracks at the base of a standpipe with lute.

Luting mixtures are generally prepared by plant personnel according to formulas developed by each plant. The consistency (thickness) of the mixture is adjusted to suit different applications.

There are few emission factors specifically for benzene emissions at coke ovens. One test that examined emissions of door leaks detected benzene in the emissions.⁴² The coke oven doors being tested were controlled with a collecting device, which then fed the collected emissions to a wet electrostatic precipitator. Tests at the precipitator inlet showed benzene concentrations of 1.9×10^{-7} to 6.2×10^{-7} lb/ft³ (1 to 3 parts per million [ppm] or about 3 to 10 milligrams per cubic meter [Mg/m³]). These data translated into an estimated benzene emission factor of 1.3 lb to 5.3 lb (0.6 to 2.4 kilograms [kg]) benzene per hour of operation for coke oven doors. In addition to coke oven door emissions, benzene may also be emitted from the coke oven bypass stack at a rate of 22 lbs/ton of coal charged (11,000 g/Mg) uncontrolled, 0.22 lbs/ton of coal charged (110 g/Mg) controlled with flare.²⁹⁶ No additional emission factors for benzene and coke ovens were found in the literature. However, an analysis of coke oven gas indicated a benzene content of 1.3×10^{-3} to 2.2×10^{-3} lb/ft³ (21.4 to 35.8 grams per cubic meter [g/m³]).

Other potential sources of benzene emissions associated with the by-product recovery plant are given in Table 4-6, along with emission factors.^{37,43}

Equipment leaks may also contribute to benzene emissions. Emission factors for pumps, valves, etc., at furnace coke and foundry coke by-product recovery plants are shown in Tables 4-7 and 4-8, respectively.^{37,43} The following paragraphs describe the potential sources of benzene emissions listed in Tables 4-6, 4-7, and 4-8. Emission sources and control technologies are described in groups of related processes, beginning with the final cooling unit.

The final cooling unit itself is not a source of benzene because coolers are closed systems. However, the induced-draft cooling towers used in conjunction with direct-water and tar-bottom final coolers are potential sources of benzene. Benzene can be condensed in the direct-contact cooling water, and in the cooling tower, lighter components (such as benzene) will be stripped from the recirculating cooling water. The emission factor of 0.54 pound per ton (lb/ton) (270 g/Mg) coke shown in Table 4-6 was based on actual measurements of benzene concentrations and volumetric gas flow rates taken from source testing reports.³⁷

Use of a wash oil final cooler effectively eliminates the benzene emissions associated with direct water or tar bottom coolers because the wash oil is cooled by an indirect heat exchanger, thereby eliminating the need for a cooling tower.³⁷ Wash oil is separated after it leaves the heat exchanger and recirculates back through the circulation tank to the final cooler.

Coke by-product recovery plants may recover naphthalene by condensing it from the coke oven gas and separating it from the cooling water by flotation. Benzene may be emitted from most naphthalene separation and processing operations.³⁷ Vapors from naphthalene separation tanks have been reported to contain benzene, benzene homologs, and other aromatic hydrocarbons.³⁷ The emission factors for naphthalene separation and

TABLE 4-6. SUMMARY OF BENZENE EMISSION FACTORS FOR FURNACE AND
FOUNDRY COKE BY-PRODUCT RECOVERY PLANTS

| SCC and Description | Emissions Source ^a | Control Device | Emission Factor lb/ton (g/Mg) ^b | | Factor Rating |
|--|--|------------------|--|-------------------------------|------------------|
| | | | Furnace Coke | Foundry Coke | |
| 3-03-003-15 By-Product Coke - Gas By-Product Plant | Cooling Tower | | | | |
| | - Direct Water (A) ^c | Uncontrolled | 0.54 (270) | 0.40 (200) | E |
| | - Tar bottom (B) ^c | Uncontrolled | 0.14 (70) | 0.10 (51) | E |
| | Light-Oil Condenser Vent (C) | Uncontrolled | 0.18 (89) | 0.096 (48) | E |
| | | Gas Blanketing | 3.6 x 10 ⁻³ (1.8) | 1.9 x 10 ⁻³ (0.97) | E |
| | Naphthalene Separation and Processing (D) | Uncontrolled | 0.22 (110) | 0.16 (80) | E |
| | | Activated Carbon | 7.0 x 10 ⁻⁴ (0.35) | 5.0 x 10 ⁻⁴ (0.25) | E |
| | Tar-Intercepting Sump (E) | Uncontrolled | 0.019 (9.5) | 0.009 (4.5) | E |
| | Tar Dewatering (F) | Uncontrolled | 0.042 (21) | 0.020 (9.9) | E |
| | | Gas Blanketing | 8.4 x 10 ⁻⁴ (0.45) | 4 x 10 ⁻⁴ (0.2) | E |

(continued)

TABLE 4-6. CONTINUED

| SCC and Description | Emissions Source ^a | Control Device | Emission Factor lb/ton (g/Mg) ^b | | Factor Rating |
|---------------------|----------------------------------|----------------|--|-------------------------------|---------------|
| | | | Furnace Coke | Foundry Coke | |
| | Tar Decanter (G) | Uncontrolled | 0.11 (54) | 0.05 (25) | E |
| | | Gas Blanketing | 22 x 10 ⁻³ (1.1) | 1.0 x 10 ⁻³ (0.5) | E |
| | Tar Storage (H) | Uncontrolled | 0.013 (6.6) | 6.2 x 10 ⁻³ | E |
| | | Gas Blanketing | 7.6 x 10 ⁻⁴ (0.38) | 3.6 x 10 ⁻⁴ (0.18) | E |
| | Light-Oil Sump (I) | Uncontrolled | 0.03 (15) | 0.016 (8.1) | E |
| | | Gas Blanketing | 6 x 10 ⁻⁴ (0.3) | 3.2 x 10 ⁻⁴ (0.16) | E |
| | Light-Oil Storage (J) | Uncontrolled | 0.012 (5.8) | 6.2 x 10 ⁻³ (3.1) | E |
| | | Gas Blanketing | 2.4 x 10 ⁻⁴ (0.12) | 1.2 x 10 ⁻⁴ (0.06) | E |
| | BTX Storage (K) ^d | Uncontrolled | 0.012 (5.8) | 6.2 x 10 ⁻³ (3.1) | E |
| | | Gas Blanketing | 2.4 x 10 ⁻⁴ (0.12) | 1.2 x 10 ⁻⁴ (0.06) | E |
| | Benzene Storage (L) ^d | Uncontrolled | 0.0116 (5.8) | 6.2 x 10 ⁻³ (3.1) | E |
| | | Gas Blanketing | 2.4 x 10 ⁻⁴ (0.12) | 1.2 x 10 ⁻⁴ (0.06) | E |

(continued)

TABLE 4-6. CONTINUED

| SCC and Description | Emissions Source ^a | Control Device | Emission Factor lb/ton (g/Mg) ^b | | Factor Rating |
|---------------------|--------------------------------------|----------------|--|------------------------------|---------------|
| | | | Furnace Coke | Foundry Coke | |
| | Flushing-Liquor Circulation Tank (M) | Uncontrolled | 0.026 (13) | 0.019 (9.5) | E |
| | | Gas Blanketing | 5.2×10^{-4} (0.26) | 3.8×10^{-4} (0.19) | E |
| | Excess-Ammonia Liquor Tank (N) | Uncontrolled | 2.8×10^{-3} | 2.0×10^{-3} | E |
| | | Gas Blanketing | 5.6×10^{-5} (0.028) | 4.0×10^{-5} (0.020) | E |
| | Wash-Oil Decanter (O) | Uncontrolled | 7.6×10^{-3} (3.8) | 4.2×10^{-3} (2.1) | E |
| | | Gas Blanketing | 1.5×10^{-4} (0.076) | 8.2×10^{-5} (0.041) | E |
| | Wash-Oil Circulation Tank (P) | Uncontrolled | 7.6×10^{-3} (3.8) | 4.2×10^{-3} (2.1) | E |
| | | Gas Blanketing | 1.5×10^{-4} (0.076) | 8.2×10^{-5} (0.041) | E |

Source: Reference 296.

^a Source identification letters correspond to locations identified in Figure 4-7.

^b Emission factors are expressed as g benzene emitted per Mg coke produced.

^c Usually only smaller plants use direct-water final cooler; all final coolers are shown as one unit in Figure 4-7.

^d Not all plants separate BTX or benzene. Therefore, all product storage is indicated in one box on the diagram in Figure 4-7.

TABLE 4-7. SUMMARY OF BENZENE EMISSION FACTORS FOR EQUIPMENT LEAKS AT
FURNACE COKE BY-PRODUCT RECOVERY PLANTS

| SCC and Description | Emissions Source | Control (% efficiency) | Emission Factor lb/source day (kg/source day) ^{a,b} | | Factor Rating |
|--|-------------------------|-------------------------------------|---|--|------------------|
| | | | Light Oil BTX Recovery ^c | Light Oil Recovery, Benzene Refining ^c | |
| 3-03-003-15 By-Product Coke - Gas By-Product Recovery | Valves | Uncontrolled | 0.4 (0.18) | 0.49 (0.22) | U |
| | | Quarterly inspection (63) | 0.15 (0.07) | 0.18 (0.08) | U |
| | | Monthly inspection (72) | 0.11 (0.05) | 0.13 (0.06) | U |
| | | Use sealed bellows valves (100) | -- | -- | |
| | Pumps | Uncontrolled | 4.2 (1.9) | 5.1 (2.3) | U |
| | | Quarterly inspection (71) | 1.2 (0.55) | 1.5 (0.67) | U |
| | | Monthly inspection (83) | 0.71 (0.32) | 0.86 (0.39) | U |
| | | Use dual mechanical seals (100) | -- | -- | |
| | Exhausters | Uncontrolled | 0.62 (0.28 ^c) | 0.62 (0.28 ^c) | U |
| | | Quarterly inspection (55) | 0.29 (0.13) | 0.29 (0.13) | U |
| | | Monthly inspection (64) | 0.22 (0.10) | 0.22 (0.10) | U |
| | | Use degassing reservoir vents (100) | -- | -- | |
| | Pressure Relief Devices | Uncontrolled | 6.0 (2.7) | 7.5 (3.4) | U |
| | | Quarterly inspection (44) | 3.3 (1.5) | 4.2 (1.9) | U |
| | | Monthly inspection (52) | 2.9 (1.3) | 3.5 (1.6) | U |
| | | Use rupture disk system (100) | -- | -- | |
| | Sampling Connections | Uncontrolled | 0.55 (0.25) | 0.68 (0.31) | U |
| | | Closed-purge sampling (100) | -- | -- | |

(continued)

TABLE 4-7. CONTINUED

| SCC and Description | Emissions Source | Control (% efficiency) | Emission Factor lb/source day (kg/source day) ^{a,b} | | Factor Rating |
|---------------------|------------------|------------------------|---|--|------------------|
| | | | Light Oil BTX Recovery ^c | Light Oil Recovery, Benzene Refining ^c | |
| | Open-ended Lines | Uncontrolled | 0.084 (0.038) | 0.104 (0.047) | U |
| | | Plug or cap (100%) | -- | -- | |

Source: Reference 37.

^a Factors are based on the total VOC emissions from petroleum refineries and the percent of benzene in light oil and refined benzene.

^b Factors are expressed as lb emitted per source day (kg benzene emitted per source day).

^c Emission factors are presented for two different types of coke by-product recovery plants, but are not representative of any particular plant.

TABLE 4-8. SUMMARY OF BENZENE EMISSION FACTORS FOR EQUIPMENT LEAKS AT FOUNDRY
COKE BY-PRODUCT RECOVERY PLANTS

| SCC and Description | Emissions Source | Control (% efficiency) | Emission Factor lb/source day (kg/source day) ^{a,b} | | Factor Rating |
|--|-------------------------|-------------------------------------|---|--|------------------|
| | | | Light Oil BTX Recovery ^c | Light Oil Recovery, Benzene Refining ^c | |
| 3-03-003-15 By-Product Coke - Gas By-Product Recovery | Valves | Uncontrolled | 0.35 (0.16) | 0.44 (0.20) | U |
| | | Quarterly inspection (63) | 0.13 (0.06) | 0.15 (0.07) | U |
| | | Monthly inspection (72) | 0.09 (0.04) | 0.13 (0.06) | U |
| | | Use sealed bellows valves (100) | -- | -- | |
| | Pumps | Uncontrolled | 3.7 (1.7) | 4.6 (2.1) | U |
| | | Quarterly inspection (71) | 1.1 (0.5) | 1.3 (0.6) | U |
| | | Monthly inspection (83) | 0.66 (0.3) | 0.88 (0.4) | U |
| | | Use dual mechanical seals (100) | -- | -- | |
| | Exhausters | Uncontrolled | 0.55 (0.25) | 0.55 (0.25) | U |
| | | Quarterly inspection (55) | 0.24 (0.11) | 0.24 (0.11) | U |
| | | Monthly inspection (64) | 0.20 (0.09) | 0.20 (0.09) | U |
| | | Use degassing reservoir vents (100) | -- | -- | |
| | Pressure Relief Devices | Uncontrolled | 5.5 (2.5) | 6.8 (3.1) | U |
| | | Quarterly inspection (44) | 3.1 (1.4) | 3.7 (1.7) | U |
| | | Monthly inspection (52) | 2.6 (1.2) | 3.3 (1.5) | U |
| | | Use rupture disk system (100) | -- | -- | |
| | Sampling Connections | Uncontrolled | 0.51 (0.23) | 0.62 (0.28) | U |
| | | Plug or cap (100) | -- | -- | |

(continued)

TABLE 4-8. SUMMARY OF BENZENE EMISSION FACTORS FOR EQUIPMENT LEAKS AT FOUNDRY
COKE BY-PRODUCT RECOVERY PLANTS

| SCC and Description | Emissions Source | Control (% efficiency) | Emission Factor lb/source day (kg/source day) ^{a,b} | | Factor Rating |
|---------------------|------------------|------------------------|---|--|------------------|
| | | | Light Oil BTX Recovery ^c | Light Oil Recovery, Benzene Refining ^c | |
| | Open-ended Lines | Uncontrolled | 0.077 (0.035) | 0.95 (0.043) | U |
| | | Closed-purge sampling | (100) | -- | |

Source: Reference 37.

^a Factors for foundry coke are drawn from Reference 43.

^b Factors are expressed in terms of lb (kg) of benzene emitted per source day.

^c Emission factors are presented for two different types of foundry coke by-product recovery plants, but are not representative of any particular plant.

"--" = Data not available.

processing shown in Table 4-6 are based on source testing data from a flotation unit, drying tank, and melt pit at a coke by-product recovery plant.³⁷

Benzene may also be emitted from the light oil plant, which includes the light-oil condenser vent, light oil decanter, storage tank, intercepting sumps, the wash-oil decanter, wash-oil circulation tank(s), and BTX storage. A control technique required by the benzene NESHAP is the use of gas blanketing with clean coke oven gas from the gas holder (or battery underfire system).⁴⁴ With this technology, a positive (or negative) pressure blanket of clean coke oven gas is piped to the light oil plant and the enclosed sources are connected to the blanketing line. Using a series of piping connections and flow inducing devices (if necessary), vapor emissions from the enclosed sources are transported back into the clean gas system (the coke-oven battery holder, the collecting main, or another point in the by-product recovery process).

Ultimate control of the vapors is accomplished by the combustion of the coke oven gas.³⁷ Such systems are currently in use at some by-product recovery plants and reportedly have operated without difficulty. Examples of gases that may be used as the gas blanket include dirty or clean coke gas, nitrogen, or natural gas.³⁷ The control efficiency is estimated to be 98 percent.^{37,44} The control technique required by the benzene NESHAP for the light oil sump is a tightly fitting, gasketed cover with an estimated 96-percent efficiency.⁴⁴ The emission factors for benzene sources in the light oil plant shown in Table 4-6 are based on source tests.³⁷

Sources of benzene emissions from tar processing include the tar decanter, the tar-intercepting sump, tar dewatering and storage, and the flushing-liquor circulation tank. Emission factors for these sources are shown in Table 4-6.

Benzene emissions from the tar decanter are sensitive to two operating practices: residence time in the separator and optimal heating of the decanter.³⁷ These two variables should be kept in mind when using the emission factors presented in Table 4-6.

Benzene is emitted from tar decanters through vents. Coke oven gas can be mechanically entrained with the tar and liquor that are fed into the decanter. Because tar is fed into the decanter at a slightly higher pressure, the coke oven gas will build up in the decanter if it is not vented.³⁷ Emissions were measured at tar decanters at several locations in the United States and the emission factor shown in Table 4-6 is the average of the test values.³⁷

The water that separates from the tar in the decanter is flushing liquor, which is used to cool the gas leaving the coke oven. Excess flushing liquor is stored in the excess ammonia liquor tank. Benzene may be emitted from the flushing liquor circulation tank and the excess ammonia liquor tank. The emission factor of 0.026 lb benzene/ton (13 g benzene/Mg) coke produced was derived from a source test of fugitive emissions from a primary cooler condensate tank. It was assumed that the condensate tank was similar in design and in liquids stored as the ammonia liquor and the flushing liquor circulation tanks.²⁹⁶ The actual benzene emission rate from the flushing liquor circulation tank and excess ammonia liquor tank depends on the number of tanks, the number of vents, and the geometry of the tanks.³⁷

The tar-intercepting sump is a type of decanter that accepts light tar and condensate from the primary cooler. Some of this condensate may be used to make up flushing liquor and some may be forwarded to ammonia recovery.³⁷ No significant benzene emissions have been identified from the recovery of ammonia, but benzene can be emitted from the intercepting sump. An emission factor of 0.019 lb/ton (9.5 g benzene/Mg) coke was reported in the literature.²⁹⁶

Tar dewatering may be accomplished by steam heating or centrifugal separation or a combination of the two methods. Use of centrifugal separation will probably not be a source of benzene emissions directly, but benzene may be emitted as a fugitive emission if storage vessels are used.³⁹ In steam heating, benzene could be driven off in the vapors. The emission factor for tar dewatering in Table 4-6 was derived by averaging three factors (0.082, 0.019, and 0.0258 lb benzene/ton coke [41, 9.5, and 12.9 g benzene/Mg

coke]) based on source tests at tar dewatering tanks.³⁷ Gas blanketing is the control technology required by the benzene NESHAP for tar processing.

The final source of benzene emissions at coke by-product recovery plants is leaks from equipment such as pumps, valves, exhausters, pressure relief devices, sampling connection systems, and open-ended lines. Emission factors are shown in Tables 4-7 and 4-8 and are based on emission factors from a comprehensive survey of petroleum refineries and the percent of benzene in the liquid associated with each type of equipment.³⁷ Two different sets of emission factors are presented, one set for a plant practicing light oil and BTX recovery and one set for a plant producing refined benzene in addition to light oil. Emission factors for exhausters were derived by multiplying the VOC emission factor for compressors in hydrogen service and refineries by 0.235, the measured ratio of benzene to nonmethane hydrocarbons present in the coke oven gas at the exhausters.³⁷

To control benzene emissions from process vessels, storage tanks, and tar-interrupting sumps as required by the benzene NESHAP, all openings must be enclosed or sealed. All gases must be routed to a gas collection system (or similar configuration) where the benzene in the gas will be removed or destroyed. Alternately, the gases may be routed through a closed vent system to a carbon absorber or vapor incinerator that is at least 98 percent efficient. See Section 4.5 for a discussion of these types of process control devices.⁴⁴ The control techniques required by the benzene NESHAP to control benzene emissions from equipment leaks are presented in Table 4-9.

For the nonrecovery process, benzene emissions for coal charging are 3.6×10^{-5} lb/ton of coal charged (1.8×10^{-2} g/Mg). Emissions from pushing and quenching are expected to be similar to those from the by-product recovery process. Additional benzene emissions occur from the combustion stack of nonrecovery batteries at the rate of 5.1×10^{-4} lb/ton of coal charged (0.26 g/Mg).²⁹⁶

TABLE 4-9. TECHNIQUES TO CONTROL BENZENE EMISSIONS FROM
EQUIPMENT LEAKS REQUIRED BY THE BENZENE NESHA FOR COKE
BY-PRODUCT RECOVERY PLANTS

| Emission Points | Control Technique (% efficiency) |
|-----------------------------|--|
| Pumps | Monthly Inspection ^a (83) Dual Mechanical Seals (100) |
| Valves | Monthly Inspection ^a (73) Sealed-Bellows Valves (100) |
| Exhausters | Quarterly Inspections ^a (55) Degassing Reservoir Vents (100) |
| Pressure-Relief Devices | Rupture Disc System (100) |
| Sampling Connection Systems | Closed-Purge Sampling (100) |
| Open-Ended Lines | Cap or Plug (100) |

Source: Reference 44.

^a Inspection and maintenance programs include tightening seals, replacing manufacturing equipment, etc.

4.5 METHODS FOR ESTIMATING BENZENE EMISSIONS FROM EMISSION SOURCES

In this section, the sources of benzene emissions from process vents, equipment leaks, storage tanks, wastewater, and transfer operations are summarized, along with the types of controls currently available for use in the industry. In addition, an overview of methods for estimating uncontrolled and controlled emissions of benzene is presented where available. Current Federal regulations applicable to these benzene emission sources are identified. The information provided in this section is applicable to benzene production facilities (discussed earlier in this chapter) as well as to facilities that use benzene as a feedstock to produce cyclic intermediates (discussed in Chapter 5.0).

4.5.1 Process Vent Emissions, Controls, and Regulations

Benzene emissions can occur from any process vent in any chemical production operation that manufactures or uses benzene. Section 4.0 of this document contains a discussion of chemical operations that manufacture benzene, whereas Section 5.0 contains a discussion of chemical operations that use benzene as feedstock. Chemical operations that emit benzene include air oxidation processes, reactor processes, and distillation operations. In air oxidation processes, one or more chemicals are reacted with oxygen supplied as air or air enriched with oxygen to create a product. With reactor processes, one or more chemicals are reacted with another chemical (besides oxygen) and chemically altered to create one or more new products. In distillation, one or more inlet feed streams is separated into two or more outlet product streams, each product stream having component concentrations different from those in the feed streams. During separation, the more volatile components are concentrated in the vapor phase and the less volatile components in the liquid phase.⁴⁵

Calculations for estimating emissions from any of these three processes are specific to the type of vent stream and the type of control in place.

Two general types of methods are used for controlling benzene emissions from process vents: recovery devices and combustion devices. Examples of each type of control device that can be used to comply with air pollution control standards, along with its estimated control efficiency, are summarized in Tables 4-10 and 4-11 and discussed briefly below.⁴⁵ The reader should keep in mind that the most appropriate recovery control device, as well as its effectiveness, is highly dependent upon flow rate, concentration, chemical and physical properties of the vent stream, contaminants present, and stream temperature. To achieve optimal control efficiency with recovery devices, several stream characteristics must remain within a certain range. Combustion control devices are less dependent upon these process and vent stream characteristics; however, combustion temperature and stream flow must remain within a certain range to ensure complete combustion.⁴⁶

TABLE 4-10. CONTROL TECHNOLOGIES THAT FORM THE BASIS OF AIR POLLUTION CONTROL STANDARDS

| Type | Control Levels Achievable | Design Conditions to Meet Control Level | Comments |
|------------------------------------|---------------------------|--|---|
| Flares | ≥ 98% | <ul style="list-style-type: none"> • Flame present at all times - monitor pilot • Non-assisted Flares - >200 Btu/scf heating value, and 60 ft/sec (18 m/sec) maximum exit velocity • Air and Steam Assisted Flares - >300 Btu/scf heating value, and maximum exit velocity based on Btu content formula | <ul style="list-style-type: none"> • Destroys rather than recovers organics • Smoking allowed for 5 min/2 hr • Not used on corrosive streams |
| Industrial Boilers/Process Heaters | ≥ 98% | <ul style="list-style-type: none"> • Vent stream directly into flame | <ul style="list-style-type: none"> • Destroys rather than recovers organics |
| Thermal Oxidation | ≥ 98%, or 20 ppm | <ul style="list-style-type: none"> • 1600°F (871 °C) Combustion temperature • 0.75 sec. residence • For halogenated streams 2000°F (1093 °C), 1.0 sec. and use a scrubber on outlet • Proper mixing | <ul style="list-style-type: none"> • Destroys rather than recovers organics • May need vapor holder on intermittent streams |
| Adsorption | ≥ 95% | <ul style="list-style-type: none"> • Adequate quantity and appropriate quality of carbon • Gas stream receives appropriate conditioning (cooling, filtering) • Appropriate regeneration and cooling of carbon beds before breakthrough occurs | <ul style="list-style-type: none"> • Most efficient on streams with low relative humidity (<50 percent). • Recovers organics |

Source: Reference 45.

TABLE 4-11. OTHER CONTROL TECHNOLOGIES THAT CAN BE USED
TO MEET STANDARDS

| Type | Estimated Control Level | Critical Variables That Affect Control Level | Comments |
|---------------------|-------------------------|--|---|
| Catalytic Oxidation | up to 98% | <ul style="list-style-type: none"> Dependent on compounds, temp. and catalyst bed size | <ul style="list-style-type: none"> Destroys rather than recovers organics Technical limitations include particulate or compounds that poison catalysts |
| Absorption | 50 to 95% | <ul style="list-style-type: none"> Solubility of gas stream in the absorbent Good contact between absorbent and gas stream | <ul style="list-style-type: none"> Appropriate absorbent needed may not be readily available Disposal of spent absorbent may require special treatment procedures, and recovery of organic from absorbent may be time consuming Preferable on concentrated streams |
| Condensation | 50 to 95% | <ul style="list-style-type: none"> Proper design of the heat exchanger Proper flow and temperature of coolant | <ul style="list-style-type: none"> Preferable on concentrated streams Recovers organics |

Source: Reference 45.

Three types of recovery devices have been identified for controlling benzene emissions: condensation, absorption, and adsorption. With a condensation-type recovery device, all or part of the condensible components of the vapor phase are converted to a liquid phase. Condensation occurs as heat from the vapor phase is transferred to a cooling medium. The most common type of condensation device is a surface condenser, where the coolant and vapor phases are separated by a tube wall and never come in direct contact with each other. Efficiency is dependent upon the type of vapor stream entering the condenser and the flow rate and temperature of the cooling medium. Condenser efficiency varies from 50 to 95 percent. Stream temperature and the organic concentration level in the stream must remain within a certain range to ensure optimal control efficiency.⁴⁶

In absorption, one or more components of a gas stream are selectively transferred to a solvent liquid. Control devices in this category include spray towers, venturi scrubbers, packed columns, and plate columns. Absorption efficiency is dependent upon the type of solvent liquid used, as well as design and operating conditions. Absorption is desirable if there is a high concentration of compound in the vent stream that can be recovered for reuse. For example, in the manufacture of monochlorobenzene, absorbers are used to recover benzene for reuse as a feedstock.⁴⁶ Stream temperature, specific gravity (the degree of adsorbing liquid saturation), and the organic concentration level must remain within a certain range to ensure optimal control efficiency.⁴⁶ Absorbers are generally not used on streams with VOC concentrations below 300 ppmv.⁴⁵ Control efficiencies vary from 50 to 95 percent.⁴⁵

In adsorption, the process vent gas stream contains a component (adsorbate) that is captured on a solid-phase surface (adsorbent) by either physical or chemical adsorption mechanisms. Carbon adsorbers are the most commonly used adsorption method. With carbon adsorption, the organic vapors are attracted to and physically held on granular activated carbon through intermolecular (van der Waals) forces. The two adsorber designs are fixed-bed and fluidized-bed. Fixed-bed adsorbers must be regenerated periodically to desorb the collected organics. Fluidized-bed adsorbers are continually regenerated.⁴⁶

Adsorption efficiency can be 95 percent for a modern, well-designed system. Removal efficiency depends upon the physical properties of the compounds in the offgas, the gas stream characteristics, and the physical properties of the adsorbent. Stream mass flow during regeneration, the temperature of the carbon bed, and organic concentration level in the stream must remain within a certain range to ensure optimal control efficiency.⁴⁶ Adsorbers are not recommended for vent streams with high VOC concentrations.⁴⁵

Four types of combustion devices are identified for control of benzene emissions from process vents: flares, thermal oxidizers, boilers and process heaters, and catalytic oxidizers. A combustion device chemically converts benzene and other organics to CO₂ and water. If combustion is not complete, the organic may remain unaltered or be converted to another organic chemical, called a product of incomplete combustion. Combustion temperature and stream flow must remain within a certain range to ensure complete combustion.⁴⁶

A flare is an open combustion process that destroys organic emissions with a high-temperature oxidation flame. The oxygen required for combustion is provided by the air around the flame. Good combustion is governed by flame temperature, residence time of the organics in the combustion zone, and turbulent mixing of the components to complete the oxidation reaction. There are two main types of flares: elevated and ground flares. A combustion efficiency of at least 98 percent can be achieved with such control.⁴⁶

A thermal oxidizer is usually a refractory-lined chamber containing a burner (or set of burners) at one end. The thermal oxidation process is influenced by residence time, mixing, and temperature. Unlike a flare, a thermal oxidizer operates continuously and is not suited for intermittent streams. Because it operates continuously, auxiliary fuel must be used to maintain combustion during episodes in which the organic concentration in the process vent stream is below design conditions. Based on new technology, it has been determined that all new thermal oxidizers are capable of achieving at least 98 percent destruction efficiency or a 20 parts per million by volume (ppmv) outlet concentration, based on operation at 870°C (1,600°F) with a 0.75-second residence time.⁴⁶

Industrial boilers and process heaters can be designed to control organics by combining the vent stream with the inlet fuel or by feeding the stream into the boiler or stream through a separate burner. An industrial boiler produces steam at high temperatures. A process heater raises the temperature of the process stream as well as the superheating steam at temperatures usually lower than those of an industrial boiler. Greater than 99 percent control efficiency is achievable with these combustion devices.⁴⁶

By using catalysts, combustion can occur at temperatures lower than those used in thermal incineration. A catalytic oxidizer is similar to a thermal incinerator except that it incorporates the use of a catalyst. Combustion catalysts include platinum, platinum alloys, copper oxide, chromium, and cobalt. Catalytic oxidizers can achieve destruction efficiencies of 98 percent or greater.⁴⁶

Biofiltration is another type of VOC control. In biofiltration, process exhaust gases are passed through soil on compost beds containing micro organisms, which convert VOC to carbon dioxide, water, and mineral salts.⁴⁷

Table 4-12 presents a comparison of the VOC control technologies (excluding combustion) that are discussed in this section.⁴⁷

Process vents emitting benzene and other VOC that are discussed in Sections 4.1 through 4.4 and in Section 5.0 are affected by one or more of the following six Federal regulations:

1. “National Emission Standards for Organic Hazardous Air Pollutants from the Synthetic Organic Chemical Manufacturing Industry,” promulgated April 22, 1994.⁴⁸
2. “National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries,” promulgated August 18, 1995.⁴⁹

TABLE 4-12. COMPARISON OF VOC CONTROL TECHNOLOGIES

| Control Technology | Applicable Concentration Range, ppm | Capacity Range, cfm | Removal Efficiency | Secondary Wastes | Advantages | Limitations and Contradictions |
|---------------------|-------------------------------------|---------------------|--------------------|---------------------------------|---|--|
| Thermal Oxidation | 100-2,000 | 1,000-500,000 | 95-99+% | Combustion products | Up to 94% energy recovery is possible. | Halogenated compounds may require additional control equipment downstream. Not recommended for batch operations. |
| Catalytic Oxidation | 100-2,000 | 1,000-100,000 | 90-95% | Combustion products | Up to 70% energy recovery is possible. | Thermal efficiency suffers with swings in operating conditions. Halogenated compounds may require additional control equipment downstream. Certain compounds can poison the catalyst (lead, arsenic, phosphorous, chlorine, sulfur, particulate matter). |
| Condensation | >5,000 | 100-20,000 | 50-90% | Condensate | Product recovery can offset annual operating costs. | Not recommended for materials with boiling point <100° F. Condensers are subject to scale buildup which can cause fouling. |
| Carbon Adsorption | 20-5,000 | 100-60,000 | 90-98% | Spent carbon; collected organic | Product recovery can offset annual operating costs. Can be used as a concentrator in conjunction with another type of control device. Works well with cyclic processes. | Not recommended for streams with relative humidity <50%. Ketones, aldehydes, and esters clog the pores of the carbon, decreasing system efficiency. |

(continued)

TABLE 4-12. CONTINUED

| Control Technology | Applicable Concentration Range, ppm | Capacity Range, cfm | Removal Efficiency | Secondary Wastes | Advantages | Limitations and Contradictions |
|--------------------|-------------------------------------|---------------------|--------------------|-------------------------------------|---|--|
| Absorption | 500-5,000 | 2,000-100,000 | 95-98% | Wastewater; Captured particulate | Product recovery can offset annual operating costs. | Might require exotic scrubbing media. Design could be difficult in the event of lack of equilibrium data. Packing is subject to plugging and fouling if particulates are in the gas stream. Scale formation from adsorbent/adsorber interaction can occur. |
| Biofiltration | 0-1,000 | <90,000 | 80-99% | Disposal of spent compost beds. | Efficient for low concentration streams. Low operating costs. | Large amount of space may be required. Microorganisms are effective only in the 50 to 100 °F temperature range and may be killed if proper bed moisture content and pH is not maintained. |

Source: Reference 47.

3. “Standards of Performance for New Stationary Sources; Volatile Organic Compound (VOC) Emissions from the Synthetic Organic Chemical Manufacturing Industry (SOCMI) Air Oxidation,” promulgated July 1, 1994.⁵⁰
4. “Standards of Performance for New Stationary Sources; Volatile Organic Compound (VOC) Emissions from the Synthetic Organic Chemical Manufacturing Industry (SOCMI) Distillation Operations,” promulgated July 1, 1994.⁵¹
5. “Standards of Performance for New Stationary Sources; Volatile Organic Compound (VOC) Emissions from the Synthetic Organic Chemical Manufacturing Industry (SOCMI) Reactor Processes,” promulgated July 1, 1994.⁵²
6. “National Emission Standards for Benzene Emissions from Coke By-Product Recovery Plants, promulgated October 27, 1993.”⁵³

In general, for the affected facilities subject to these six regulations, use of the recovery devices and combustion devices discussed above is required. Tables 4-10 and 4-11 present a summary of those controls and the required operating parameters and monitoring ranges needed to ensure that the required control efficiency is being achieved.

4.5.2 Equipment Leak Emissions, Controls, and Regulations

Equipment leak emissions occur from process equipment components whenever the liquid or gas streams leak from the equipment. Equipment leaks can occur from the following components: pump seals, process valves, compressor seals and safety relief valves, flanges, open-ended lines, and sampling connections. The following approaches for estimating equipment leak emissions are presented in the EPA publication *Protocol for Equipment Leak Emission Estimates*:⁵⁴

- Average emission factor approach;
- Screening ranges approach;
- EPA correlation approach; and
- Unit-specific correlation approach.

The approaches differ in complexity; however, greater complexity usually yields more accurate emissions estimates.

The simplest method, the average emission factor approach, requires that the number of each component type be known. For each component, the benzene content of the stream and the time the component is in service are needed. This information is then multiplied by the EPA's average emission factors for the SOCFI shown in Table 4-13.⁵⁴ Refinery average emission factors are shown in Table 4-14; marketing terminal average emission factors are shown in Table 4-15; and oil and gas production average emission factors are shown in Table 4-16.⁵⁴ This method is an improvement on using generic emissions developed from source test data, inventory data, and/or engineering judgement. However, this method should only be used if no other data are available because it may result in an overestimation or underestimation of actual equipment leak emissions. For each component, estimated emissions are calculated as follows:

$$\left[\begin{array}{c} \text{No. of} \\ \text{equipment} \\ \text{components} \end{array} \right] \times \left[\begin{array}{c} \text{Weight \%} \\ \text{benzene} \\ \text{in the stream} \end{array} \right] \times \left[\begin{array}{c} \text{Component -} \\ \text{specific} \\ \text{emission factor} \end{array} \right] \times \left[\begin{array}{c} \text{No. hr/yr in} \\ \text{benzene service} \end{array} \right]$$

To obtain more accurate equipment leak emission estimates, one of the more complex estimation approaches should be used. These approaches require that some level of emissions measurement for the facility's equipment components be collected. These are described briefly, and the reader is referred to the EPA protocol document for the calculation details.

The screening ranges approach (formerly known as the leak/no leak approach) is based on a determination of the number of leaking and non-leaking components. This approach may be applied when screening data are available as either "greater than or equal to 10,000 ppmv" or as "less than 10,000 ppmv." Emission factors for these two ranges of screening values are presented in Table 4-17 for SOCFI screening; Table 4-18 for refinery screening, Table 4-19 for marketing terminal screening, and Table 4-20 for oil and gas production screening.⁵⁴

TABLE 4-13. SOCMI AVERAGE TOTAL ORGANIC COMPOUND EMISSION FACTORS FOR EQUIPMENT LEAK EMISSIONS^a

| Equipment Type | Service | Emission Factor ^b |
|-------------------------|--------------|------------------------------|
| | | lb/hr/source (kg/hr/source) |
| Valves | Gas | 0.01313 (0.00597) |
| | Light liquid | 0.00887 (0.00403) |
| | Heavy liquid | 0.00051 (0.00023) |
| Pump seals ^c | Light liquid | 0.0438 (0.0199) |
| | Heavy liquid | 0.01896 (0.00862) |
| Compressor seals | Gas | 0.502 (0.228) |
| Pressure relief valves | Gas | 0.229 (0.104) |
| Connectors | All | 0.00403 (0.00183) |
| Open-ended lines | All | 0.0037 (0.0017) |
| Sampling connections | All | 0.0330 (0.0150) |

Source: Reference 54.

^a The emission factors presented in this table for gas valves, light liquid valves, light liquid pumps, and connectors are revised SOCMI average emission factors.

^b These factors are for total organic compound emission rates.

^c The light liquid pump seal factor can be used to estimate the leak rate from agitator seals.

The EPA correlation approach offers an additional refinement to estimating equipment leak emissions by providing an equation to predict mass emission rate as a function of screening value for a specific equipment type. The EPA correlation approach is preferred when actual screening values are available. Correlation operations for SOCMI, refinery, marketing terminals, and oil and gas production along with respective correlation curves are provided in Reference 54.

The unit-specific correlation approach requires the facility to develop its own correlation equations and requires more rigorous testing, bagging, and analyzing of equipment leaks to determine mass emission rates.

Appendix A of the EPA protocol document provides example calculations for each of the approaches described above.

TABLE 4-14. REFINERY AVERAGE EMISSION FACTORS

| Equipment type | Service | Emission Factor (kg/hr/source) ^a |
|-------------------------|--------------|--|
| Valves | Gas | 0.0268 |
| | Light Liquid | 0.0109 |
| | Heavy Liquid | 0.00023 |
| Pump seals ^b | Light Liquid | 0.114 |
| | Heavy Liquid | 0.021 |
| Compressor seals | Gas | 0.636 |
| Pressure relief valves | Gas | 0.16 |
| Connectors | All | 0.00025 |
| Open-ended lines | All | 0.0023 |
| Sampling connections | All | 0.0150 |

Source: Reference 54.

^a These factors are for non-methane organic compound emission rates.

^b The light liquid pump seal factor can be used to estimate the leak rate from agitator seals.

Although no specific information on controls of fugitive emissions used by the industry was identified, equipment components in benzene service will have some controls in place. Generally, control of fugitive emissions will require the use of sealless or double mechanical seal pumps and an inspection and maintenance program, as well as replacement of leaking valves and fittings. Typical controls for equipment leaks are listed in Table 4-21.⁵⁵ Some leakless equipment is available, such as leakless valves and sealless pumps.⁵⁵

Equipment leak emissions are regulated by the National Emission Standard for Equipment Leaks (Fugitive Emission Sources) of Benzene promulgated in June 6, 1984.⁵⁶ This standard applies to sources that are intended to operate in benzene service, such as pumps, compressors, pressure relief devices, sampling connection systems, open-ended valves or lines, valves, flanges and other connectors, product accumulator vessels, and control devices or systems required by this subpart.

TABLE 4-15. MARKETING TERMINAL AVERAGE EMISSION FACTORS

| Equipment Type | Service | Emission Factor (kg/hr/source) ^a |
|--|--------------|--|
| Valves | Gas | 1.3x10 ⁻⁵ |
| | Light Liquid | 4.3x10 ⁻⁵ |
| Pump seals | Gas | 6.5x10 ⁻⁵ |
| | Light Liquid | 5.4x10 ⁻⁴ |
| Others (compressors and others) ^b | Gas | 1.2x10 ⁻⁴ |
| | Light Liquid | 1.3x10 ⁻⁴ |
| Fittings (connectors and flanges) ^c | Gas | 4.2x10 ⁻⁵ |
| | Light Liquid | 8.0x10 ⁻⁶ |

Source: Reference 54.

^a These factors are for total organic compound emission rates (including non-VOC such as methane and ethane).

^b The "other" equipment type should be applied for any equipment type other than fittings, pumps, or valves.

^c "Fittings" were not identified as flanges or non-flanged connectors; therefore, the fitting emissions were estimated by averaging the estimates from the connector and the flange correlation equations.

Each owner or operator subject to Subpart J shall comply with the requirement of the National Emission Standard for Equipment Leaks promulgated in June 6, 1984.⁵⁷ The provisions of this subpart apply to the same sources mentioned above that are intended to operate in volatile hazardous air pollutant (VHAP) service. Benzene is a VHAP.

The SOCM I New Source Performance Standards promulgated in October 18, 1983⁵⁸ also apply to equipment leak emissions. These standards apply to VOC emissions at affected facilities that commenced construction, modification, or reconstruction after January 5, 1981.

Equipment leak emissions from Coke by-product recovery plants are regulated by the National Emission Standard for Benzene Emissions from Coke By-Product Recovery Plants promulgated in September 14, 1989.⁵³ These standards apply to the same sources (equipment leak components) as indicated in Subpart J, and V of Part 61.

TABLE 4-16. OIL AND GAS PRODUCTION OPERATIONS AVERAGE
EMISSION FACTORS (kg/hr/source)

| Equipment Type | Service ^a | Emission Factor (kg/hr/source) ^b |
|---------------------|----------------------|--|
| Valves | Gas | 4.5×10^{-3} |
| | Heavy Oil | 8.4×10^{-6} |
| | Light Oil | 2.5×10^{-3} |
| | Water/Oil | 9.8×10^{-5} |
| Pump seals | Gas | 2.4×10^{-3} |
| | Heavy Oil | NA |
| | Light Oil | 1.3×10^{-2} |
| | Water/Oil | 2.4×10^{-5} |
| Others ^c | Gas | 8.8×10^{-3} |
| | Heavy Oil | 3.2×10^{-5} |
| | Light Oil | 7.5×10^{-3} |
| | Water/Oil | 1.4×10^{-2} |
| Connectors | Gas | 2.0×10^{-4} |
| | Heavy Oil | 7.5×10^{-6} |
| | Light Oil | 2.1×10^{-4} |
| | Water/Oil | 1.1×10^{-4} |
| Flanges | Gas | 3.9×10^{-4} |
| | Heavy Oil | 3.9×10^{-7} |
| | Light Oil | 1.1×10^{-4} |
| | Water/Oil | 2.9×10^{-6} |
| Open-ended lines | Gas | 2.0×10^{-3} |
| | Heavy Oil | 1.4×10^{-4} |
| | Light Oil | 1.4×10^{-3} |
| | Water/Oil | 2.5×10^{-4} |

Source: Reference 54.

^a Water/Oil emission factors apply to water streams in oil service with a water content greater than 50 percent, from the point of origin to the point where the water content reaches 99 percent. For water streams with a water content greater than 99 percent, the emission rate is considered negligible.

^b These factors are for total organic compound emission rates (including non-VOC such as methane and ethane) and apply to light crude, heavy crude, gas plant, gas production, and off shore facilities. "NA" indicates that not enough data were available to develop the indicated emission factor.

^c The "other" equipment type was derived from compressors, diaphragms, drains, dump arms, hatches, instruments, meters, pressure relief valves, polished rods, relief valves, and vents. This "other" equipment type should be applied for any equipment type other than connectors, flanges, open-ended lines, pumps, or valves.

TABLE 4-17. SOCMI SCREENING VALUE RANGE TOTAL ORGANIC COMPOUND EMISSION FACTORS
FOR EQUIPMENT LEAK EMISSIONS^a

| Equipment Type | Service | ≥ 10,000 ppmv Emission Factor ^b | <10,000 ppmv Emission Factor ^b |
|-------------------------|--------------|--|---|
| | | lb/hr/source(kg/hr/source) | lb/hr/source(kg/hr/source) |
| Valves | Gas | 0.1720 (0.0782) | 0.000288 (0.000131) |
| | Light liquid | 0.1962 (0.0892) | 0.000363 (0.000165) |
| | Heavy liquid | 0.00051 (0.00023) | 0.00051 (0.00023) |
| Pump seals ^c | Light liquid | 0.535 (0.243) | 0.00411 (0.00187) |
| | Heavy liquid | 0.475 (0.216) | 0.00462 (0.00210) |
| Compressor seals | Gas | 3.538 (1.608) | 0.1967 (0.0894) |
| Pressure relief valves | Gas | 3.720 (1.691) | 0.0983 (0.0447) |
| Connectors | All | 0.249 (0.113) | 0.0001782 (0.0000810) |
| Open-ended lines | All | 0.02629 (0.01195) | 0.00330 (0.00150) |

Source: Reference 54.

^a The emission factors presented in this table for gas valves, light liquid valves, light liquid pumps, and connectors are revised SOCMI ≥ 10,000/< 10,000 ppmv emission factors.

^b These factors are for total organic compound emission rates.

^c The light liquid pump seal factors can be applied to estimate the leak rate from agitator seals.

TABLE 4-18. REFINERY SCREENING RANGES EMISSION FACTORS

| Equipment Type | Service | ≥ 10,000 ppmv Emission Factor (kg/hr/source) ^a | <10,000 ppmv Emission Factor (kg/hr/source) ^a |
|-------------------------|--------------|---|--|
| Valves | Gas | 0.2626 | 0.0006 |
| | Light Liquid | 0.0852 | 0.0017 |
| | Heavy Liquid | 0.00023 | 0.00023 |
| Pump seals ^b | Light Liquid | 0.437 | 0.0120 |
| | Heavy Liquid | 0.3885 | 0.0135 |
| Compressor seals | Gas | 1.608 | 0.0894 |
| Pressure relief valves | Gas | 1.691 | 0.0447 |
| Connectors | All | 0.0375 | 0.00006 |
| Open-ended lines | All | 0.01195 | 0.00150 |

Source: Reference 54.

^a These factors are for non-methane organic compound emission rates.

^b The light liquid pump seal factors can be applied to estimate the leak rate from agitator seals.

The hazardous organic NESHAP (or HON) equipment leak provisions promulgated on April 22, 1994, affect chemical production processes.^{59,60} The HON provisions apply to new and existing facilities and specify a control level of 90 percent.

The petroleum refineries NESHAP equipment leak provisions promulgated on August 18, 1995 affects petroleum refinery process units. The petroleum refinery provisions apply to new and existing facilities.

4.5.3 Storage Tank Emissions, Controls, and Regulations

A possible source of benzene emissions from chemical production operations that produce or use benzene are storage tanks that contain benzene. Emissions from storage tanks include "working losses" and "breathing losses." Working losses are emissions that occur while a tank is being filled (filling the tank with liquid forces organic vapors out of the tank). Breathing losses are emissions that result from expansion due to temperature changes (a higher

TABLE 4-19. MARKETING TERMINAL SCREENING RANGES
EMISSION FACTORS

| Equipment Type | Service | ≥ 10,000 ppmv Emission Factor (kg/hr/source) ^a | <10,000 ppmv Emission Factor (kg/hr/source) ^a |
|---|--------------|---|--|
| Valves | Gas | NA | 1.3x10 ⁻⁵ |
| | Light Liquid | 2.3x10 ⁻² | 1.5x10 ⁻⁵ |
| Pump seals | Light Liquid | 7.7x10 ⁻² | 2.4x10 ⁻⁴ |
| Others (compressors and others) ^b | Gas | NA | 1.2x10 ⁻⁴ |
| | Light Liquid | 3.4x10 ⁻² | 2.4x10 ⁻⁵ |
| Fittings (connectors and flanges) ^c | Gas | 3.4x10 ⁻² | 5.9x10 ⁻⁶ |
| | Light Liquid | 6.5x10 ⁻³ | 7.2x10 ⁻⁶ |

Source: Reference 54.

^a These factors are for total organic compound emission rates (including non-VOC such as methane and ethane).

"NA" indicates that not enough data were available to develop the indicated emission factors.

^b The "other" equipment type should be applied for any equipment type other than fittings, pumps, or valves.

^c "Fittings" were not identified as flanges or connectors; therefore, the fitting emissions were estimated by averaging the estimates from the connector and the flange correlation equations.

ambient temperature heats the air inside the tank, causing the air to expand and forcing organic vapors out of the tank). The calculations to estimate working and breathing loss emissions from storage tanks are complex and require knowledge of a number of site-specific factors about the storage tank for which emissions are being estimated. Equations for estimating emissions of organic compounds from storage tanks are provided in the EPA document entitled *Compilation of Air Pollutant Emission Factors (AP-42)*, Chapter 7.³³

Benzene emissions from storage tanks may be reduced with control equipment and by work practices. Various types of control equipment may be used to reduce organic emissions, including (1) storing the liquid in a storage tank with a floating deck (i.e., an internal-floating-roof tank or external-floating-roof tank), (2) equipping floating decks with additional devices to reduce emissions (e.g., applying sealing mechanisms around the perimeter of the floating deck, welding the deck seams, installing gaskets around openings and in closure devices on the floating deck), and (3) venting air emissions from a fixed-roof storage tank to a control device (e.g., a closed-vent system and a carbon adsorber, condenser, or flare). Work

TABLE 4-20. OIL AND GAS PRODUCTION OPERATIONS SCREENING RANGES
EMISSION FACTORS

| Equipment Type | Service ^a | $\geq 10,000$ ppmv Emission Factor (kg/hr/source) ^b | 10,000 ppmv Emission Factor (kg/hr/source) ^b |
|---------------------|----------------------|--|---|
| Valves | Gas | 9.8×10^{-2} | 2.5×10^{-5} |
| | Heavy Oil | NA | 8.4×10^{-6} |
| | Light Oil | 8.7×10^{-2} | 1.9×10^{-5} |
| | Water/Oil | 6.4×10^{-2} | 9.7×10^{-6} |
| Pump seals | Gas | 7.4×10^{-2} | 3.5×10^{-4} |
| | Heavy Oil | NA | NA |
| | Light Oil | 1.0×10^{-1} | 5.1×10^{-4} |
| | Water/Oil | NA | 2.4×10^{-5} |
| Others ^c | Gas | 8.9×10^{-2} | 1.2×10^{-4} |
| | Heavy Oil | NA | 3.2×10^{-5} |
| | Light Oil | 8.3×10^{-2} | 1.1×10^{-4} |
| | Water/Oil | 6.9×10^{-2} | 5.9×10^{-5} |
| Connectors | Gas | 2.6×10^{-2} | 1.0×10^{-5} |
| | Heavy Oil | NA | 7.5×10^{-6} |
| | Light Oil | 2.6×10^{-2} | 9.7×10^{-6} |
| | Water/Oil | 2.8×10^{-2} | 1.0×10^{-5} |
| Flanges | Gas | 8.2×10^{-2} | 5.7×10^{-6} |
| | Heavy Oil | NA | 3.9×10^{-7} |
| | Light Oil | 7.3×10^{-2} | 2.4×10^{-6} |
| | Water/Oil | NA | 2.9×10^{-6} |
| Open-ended lines | Gas | 5.5×10^{-2} | 1.5×10^{-5} |
| | Heavy Oil | 3.0×10^{-2} | 7.2×10^{-6} |
| | Light Oil | 4.4×10^{-2} | 1.4×10^{-5} |
| | Water/Oil | 3.0×10^{-2} | 3.5×10^{-6} |

Source: Reference 54.

^a Water/Oil emission factors apply to water streams in oil service with a water content greater than 50 percent, from the point of origin to the point where the water content reaches 99 percent. For water streams with a water content greater than 99 percent, the emission rate is considered negligible.

^b These factors are for total organic compound emission rates (including non-VOC such as methane and ethane) and apply to light crude, heavy crude, gas plant, gas production, and off shore facilities. "NA" indicates that not enough data were available to develop the indicated emission factor.

^c The "other" equipment type was derived from compressors, diaphragms, drains, dump arms, hatches, instruments, meters, pressure relief valves, polished rods, relief valves, and vents. This "other" equipment type should be applied for any equipment type other than connectors, flanges, open-ended lines, pumps, or valves.

TABLE 4-21. CONTROL TECHNIQUES AND EFFICIENCIES APPLICABLE TO EQUIPMENT LEAK EMISSIONS

| Equipment Component (Emission Source) | Control Technique | Percent Reduction ^a |
|--|---|--------------------------------|
| Pump Seals: | | |
| Packed and Mechanical | Seal area enclosure vented to a combustion device | 100 |
| | Monthly LDAR ^b | 69 |
| | Quarterly LDAR | 45 |
| Double Mechanical ^c | N/A ^d | -- |
| Compressors | Vent degassing reservoir to combustion device | 100 |
| Flanges | None available | 0 |
| Valves: | | |
| Gas | Monthly LDAR | 87 |
| | Quarterly LDAR | 67 |
| Liquid | Monthly LDAR | 84 |
| | Quarterly LDAR | 61 |
| Pressure Relief Devices | | |
| Gas | Monthly LDAR | 50 |
| | Quarterly LDAR | 44 |
| | Rupture Disk | 100 |
| Sample Connections | Closed-purge sampling | 100 |
| Open-Ended Lines | Caps on open ends | 100 |

Source: Reference 55.

^a If a negative reduction for a control technique was indicated, zero was used.

^b LDAR = Leak detection and repair, at a leak definition of 10,000 ppmv.

^c Assumes the seal barrier fluid is maintained at a pressure above the pump stuffing box pressure and the system is equipped with a sensor that detects failure of the seal and/or barrier fluid system.

^d N/A - Not applicable. There are no VOC emissions from this component.

practices that reduce organic emissions include keeping manholes and other access doors gasketed and bolted unless in use.

The control efficiencies achieved by the various types of control equipment vary. Storage tanks with internal or external floating roofs will have varying emission control efficiencies depending on the type of floating deck and seal mechanism used, as well as various other factors. The control efficiency achieved by closed-vent systems and control devices also varies, depending on the type and specific design of the control device used. For information on the control efficiencies associated with specific control devices, refer to Tables 4-10 and 4-11. The control devices applicable to reducing process vent emissions listed in these tables are also applicable to storage tanks.

Storage tanks containing benzene and other organic compounds are regulated by the four following Federal rules:

1. “National Emission Standard for Benzene Emissions from Benzene Storage Vessels;”⁶¹
2. “Standards of Performance for Volatile Organic Liquid Storage Vessels for which Construction, Reconstruction, or Modification Commenced after July 23, 1984;”⁶²
3. “National Emission Standards for Organic Hazardous Air Pollutants from the Synthetic Organic Chemical Manufacturing Industry for Process Vents, Storage Vessels, Transfer Operations, and Wastewater;”⁶³ and
4. “National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries.”⁴⁹

In combination, these four regulations generally require new and existing facilities subject to the rules to store benzene in an internal-floating-roof storage tank, an external-floating-roof storage tank, or a fixed-roof storage tank with a closed-vent system and control device that reduces emissions by 95 percent for a new facility, or 90 percent for an existing facility. Additionally, the four regulations include requirements for specific seal mechanisms and gaskets to be utilized on a floating roof, as well as certain work practices.

4.5.4 Wastewater Collection and Treatment System Emissions, Controls, and Regulations

A possible source of benzene emissions from chemical production operations that use benzene are wastewater collection and treatment systems that handle wastewater containing benzene. Benzene emissions from wastewater collection systems can originate from various types of equipment including wastewater tanks, surface impoundments, containers, drain systems, and oil-water separators. Emissions also originate from wastewater treatment systems. Equations for estimating emissions of organic compounds from wastewater collection and treatment systems are provided in the EPA document *Compilation of Air Pollutant Emission Factors (AP-42)*, Chapter 4.⁶⁴

Two control strategies can be applied to benzene emissions from wastewater. The first control strategy is waste minimization through process modifications, modification of operating practices, preventive maintenance, recycling, or segregation of waste streams. The second control strategy is to reduce the benzene content of the wastewater through treatment before the stream contacts ambient air. A complete strategy for reducing the benzene content of the wastewater includes: (1) suppression of emissions from collection and treatment system components by hard piping or enclosing the existing wastewater collection system up to the point of treatment, (2) treatment of the wastewater to remove benzene, and (3) treatment of residuals. Residuals include oil phases, condensates, and sludges from nondestructive treatment units.⁶⁵ This section will discuss the second control strategy of reducing benzene emissions by suppression and treatment.

The benzene emissions from wastewater collection and treatment systems can be controlled either by hard piping or by enclosing the transport and handling system from the point of wastewater generation until the wastewater is treated to remove or destroy the organic compounds. Suppression techniques can be broken down into four categories: collection system controls, roofs, floating membranes, and air-supported structures. These techniques can be applied to drain systems, tanks, containers, surface impoundments, and oil-water separators. Suppression of benzene emissions merely keeps the organic compounds in the wastewater until

they reach the next potential benzene emission source. Therefore, these techniques are not effective unless the benzene emissions are suppressed until the wastewater reaches a treatment device where the organic compounds are either removed or destroyed. Also, work practices, such as leak detection and repair, must be used to maintain equipment effectiveness.⁶⁵

Treatment techniques that can be used to remove or destroy benzene are steam stripping and air stripping (removal) and biological treatment (destruction). Steam and air stripping accomplish removal by stripping benzene out of the wastewater into a gas stream, which must then be controlled and vented to the atmosphere. Biological treatment destroys benzene by using microorganisms to biodegrade the benzene in the process of energy and biomass production.

Add-on controls serve to reduce benzene emissions by destroying or extracting benzene from gas phase vent streams before it is discharged to the atmosphere. Add-on controls are applicable to vents associated with collection and treatment covers, such as drain covers, fixed roofs, and air-supported structures, and with organic compound removal devices, such as air strippers and steam strippers. Add-on controls for benzene emissions are classified into four broad categories: adsorption, combustion, condensation, and absorption. The type of add-on control best suited for a particular wastewater emission source depends on the size of the source and the characteristics of the wastewater in the source.⁶⁵

The control efficiencies associated with the various types of suppression, treatment, and add-on control equipment vary. Estimating the control efficiency of emissions suppression techniques for wastewater collection systems (e.g., water seals, covers, floating roofs, and submerged fill pipes) is complex, and equations for estimating emissions from these sources are not readily available. The control efficiency associated with use of a fixed-roof or gasketed cover and a closed-vent system routed to a control device would be equivalent to the efficiency achieved by the control device. Refer to Tables 4-10 and 4-11 for a listing of control devices applicable to wastewater systems. Additionally, the control efficiencies associated with steam and air strippers and biological treatment units vary, depending on the design of the systems. Refer to the discussion below for the specific control efficiencies associated with

steam strippers and biological treatment units that would be designed to comply with existing Federal regulations.

Wastewater streams containing benzene are Federally regulated by the following rules:

1. “National Emission Standard for Benzene Waste Operations;”⁶⁶
2. “National Emission Standards for Organic Hazardous Air Pollutants from the Synthetic Organic Chemical Manufacturing Industry for Process Vents, Storage Vessels, Transfer Operations, and Wastewater” (HON);⁶³ and
3. “National Emission Standards for Hazardous Air Pollutants at Petroleum Refineries.”⁴⁹

The rules regulate benzene emissions from wastewater collection and treatment systems, and apply to new and existing facilities. Chemical production processes subject to the regulations would be required to apply many of the controls specified above for both wastewater collection and waste water treatment systems.

The rules require specific suppression equipment (e.g., roofs) and work practices (e.g., leak detection and repair) rather than specifying a suppression control efficiency that must be achieved. For add-on control devices (e.g., incinerators, adsorbers) to destroy organics vented from collection and treatment equipment, both rules require 95 percent efficiency.

For treatment, the National Emission Standard for Benzene Waste Operations⁶⁶ and the National Petroleum Refinery NESHAP⁴⁹ do not require specific treatment equipment. Instead, the rule requires the treatment process to achieve either removal or destruction of benzene in the waste system by 99 percent, or removal of benzene to less than 10 parts per million by weight (ppmw). However, the technology basis for the 99 percent efficiency standard is steam stripping.

The HON offers several different wastewater treatment compliance options. These options include concentration-based limits, pollutant reduction percentages, and an equipment standard. The equipment standard is a steam stripper with specific design criteria that would result in a 99 percent reduction in benzene emissions. The HON also allows facilities to comply with the treatment standard by using biological treatment units that achieve a 95 percent reduction of total organic hazardous air pollutants in the wastewater. (Benzene is one of the hazardous air pollutants).

4.5.5 Product Loading and Transport Operations Emissions, Controls, and Regulations

Although pipeline transfer of raw materials and products is widely used in the different industries, shipment by tank cars, tank trucks, ships, and barges is also common. The product loading and transportation of chemicals and petroleum liquids represent potential sources of evaporation losses.

Emissions from the above sources are due to loading losses, ballasting losses, and transit losses. Refer to Section 6.3 (Gasoline Marketing) of this document for information on emission factors and equations to estimate emissions from loading and transport operations, as well as information on control technology.

The HON regulates organic hazardous air pollutants (HAP) emissions from product loading and transport operations.^{59,63} The National Emission Standard for Benzene Emissions from Benzene Transfer Operations also regulates benzene transfer emissions.⁶⁷